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Fire Detection by Surface Acoustic Wave Chemical Sensor Systems

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FIRE DETECTION BY SURFACE ACOUSTIC WAVE CHEMICAL SENSOR SYSTEMS

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INTRODUCTION

During the past decade Surface Acoustic Wave (SAW) devices have shown strong promise in organic vapor or gas detection [1-6]. Efforts at NRL have focused primarily on methods to detect chemical warfare agents but more recently SAW sensors have emerged as an effective sensor technology that can be adapted to a variety of detection problems. In the present work a SAW sensor system has been developed and challenged with the vapors released when a variety of shipboard materials are thermally heated.

SAW devices operate by applying a time varying electric field to the surface of a piezoelectric material via an interdigital transducer (IDT) element lithographically patterned to the surface. SAW devices have been fabricated in two main configurations: the delay line and the resonator. The delay line configuration was for a long time the standard type used for chemical sensors, and it has been used in sensor systems developed for chemical warfare agent detection. However more recently it has shown that resonator SAW devices provide better baseline stability and lower noise levels [7,8]. SAW Resonator devices were chosen for use with the fire threat detection program.

The SAW resonator devices used in this work consist of two aluminium ITD arrays that convert electrical energy into mechanical energy (and vice versa), and a set of reflector boards on each end of a polished ST-cut quartz crystal, Fig. 1. When a time varying radio frequency potential is applied to one set of ITD's, a synchronous mechanical deformation of quartz with coincident generation of an acoustic wave in the surface of the quartz crystal results. This wave travels across the surface of the crystal and is received by the second set of ITD's which translates the wave back into an electrical signal. The wave continues across the crystal and is reflected at each end

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of the crystal surface, resulting in a standing wave developed by constructive interference of the reflected waves. The propagation of the surface acoustic wave is perturbed by the presence or accumulation of material on the surface of the SAW device and the detection of chemical species is monitored by a change in SAW frequency.

Operation of a SAW device as a chemical sensor normally involves the deposition of some chemically selective material onto the surface of the SAW device [6,9,10]. In this work thin polymer films are coated over the entire surface of the SAW device. When a vapor is exposed to the polymer-coated SAW device, it distributes between the gas and polymer phases and comes to rapid thermodynamic equilibrium, Fig. 2. The mass and modulus changes that result from vapor absorption in the polymer film perturb the propagation of the surface acoustic wave [11], and the response is monitored as a change in resonant frequency. The ratio between the concentration of the vapor in the gas phase, C_v , and the concentration of vapor in the polymer phase, C_p , is the partition coefficient, K_p , given by equation 1. The SAW device mass loading response to vapor, Δf_v , can also be related to the partition coefficient by equation 2, where the amount of polymer coating on the SAW device surface is expressed as a frequency shift, Δf_p , and δ_p is the density of the polymer coating [6].

$$K_p = C_p/C_v \quad (1)$$

$$\Delta f_v = \Delta f_p C_v K / \delta_p \quad (2)$$

The polymeric coatings typically used as SAW device coatings are not uniquely selective toward one analyte vapor but are selective toward a particular class of vapor.

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For example, polyethyleneimine (PEI), a strong hydrogen-bond basic material, may be chosen as a SAW device coating to enhance the detection of hydrogen-bond acidic solute vapors such as water or alcohols [1]. The choice of polymeric coatings for different applications will be dealt with later. To achieve high selectivity and avoid false alarms, SAW sensor systems have been designed around arrays of SAW devices, each device with a different selective polymeric coating. The array gives rise to a pattern of responses depending on the solubility properties of the coatings used [12-17] and the solubility properties of the vapors being analyzed [18]; the vapor or mixture of vapors can then be identified using pattern recognition techniques.

EXPERIMENTAL SECTIONS

1 HARDWARE DEVELOPMENT

The original prototype fabricated by Microsensors, Inc. (Bolling Green, KY) has been substantially modified, but the main components are similar to the original specifications. The system is shown schematically in Fig 3. It consists of a sensor array and driver electronics with sensor temperature control all housed in one SAW sensor array unit, a gas sampling system, a microcontroller board, a sensor interface board, and a power supply which can be either 115VAC or 12-15VDC. It comes equipped with an LCD display, a serial port, and a numeric keypad. The complete prototype system (second generation) is briefcase sized ($14\frac{1}{2} \times 12\frac{5}{8} \times 3\frac{1}{2}$ in.) and weighs approximately 10lb.

1.a SAW Sensor Array Unit

At the heart of the system is the sensor array unit (5 $\frac{3}{4}$ x5 $\frac{3}{4}$ x1 $\frac{1}{2}$ in.) which was fabricated by Femtometrics, Inc. (Costa Mesa, CA) according to NRL specifications. The array unit contains four SAW resonator cards, each with two 200 MHz SAW resonator devices. One of the SAW devices is polymer coated and is for sampling gas and the second acts as a reference and is not exposed to vapor and is hermetically sealed. The SAW devices can be individually removed and replaced in a matter of seconds, this allows different arrays to be easily tested and is an improvement over earlier prototypes in which the 4 SAW sensor array was permanently epoxied in place with no possibility of easily changing the sensor array. The driver electronics are designed such that the SAW devices operate as the resonant element in an oscillator circuit with a feedback amplifier. The signal of an individual SAW device is a frequency and the devices used are near 200 MHz. The signals of the sampling and reference devices are mixed to provide a low frequency difference signal in the kilohertz range which is easily counted by digital electronics to reflect changes in the polymer-coated SAW device. A peltier unit that can electrically cool or heat controls the temperature of the SAW devices. An aluminium block epoxied to one side of the peltier unit was employed to heat sink the peltier device to the sensor array. The other side of the the peltier was epoxied to the lid of the box and enabled easy access to the sensor array by simply removing the lid. In addition the four SAW resonator cards were mounted together as one large electronics board on spring loaded stilts. This allowed for good thermal contact between the aluminium heat sink and the sensor array without excessive pressure being applied. Thermally conductive paste was coated onto the lids of the SAW devices to better facilitate heat transfer.

1.b Microcontroller Board

The system is operated by a microcontroller board (model SBS-150) which is made by Octagon Systems Corp. (Westminster, CO) and controls the operation of valves, pumps and temperature control functions. In addition the microcontroller interprets data from the frequency counter card and provides an operator menu on the LCD display, which is accessible via a numeric keypad. The microcontroller board contains an SRAM chip which holds the operating program. The microcontroller is equipped with a serial port which is used to output data to a host computer during system development and testing, and allows the operator to read and write upgrades for the operating program. This port could also be used to connect the system to a central control system.

1.c Sensor Interface Board

The Sensor interface board which was made by Microsensors, Inc. (Bolling Green, KY) contains 4 frequency counters for the 4 SAW sensor array, and can be expanded to 6 without modification to hardware. In addition the board contains switches for the various functions that are controlled by the microcontroller board.

1.d Power Supply

The power can be supplied either by 115VAC or by a battery 12-15VDC. The use of a battery is necessary for field tests where AC power is not available or is frequently interrupted. Using a 12 Ampere-hour rechargeable battery, the system can be operated for approximately 24 hours without a recharge. Note that the size and

power requirements of the system would be dramatically reduced if hybrid electronics were used to miniaturize the electronics boards.

1.e SAW devices

SAW resonator devices (200 MHz) [7] and driver electronics were obtained from Femtometrics, Costa Mesa, CA. The SAW devices are fabricated on ST cut quartz with aluminum metallization applied by vacuum deposition, for the reflector boards and signal transducers. The SAW devices were obtained with a thin protective overlay of silicon dioxide; the silica overlay was applied to a target thickness of 30 to 50 nm. The devices are epoxy mounted on rectangular five-pin headers and gold leads attached by wire bonding, one device per header. The SAW devices are supplied with nickel lids which were modified by silver brazing a pair of stainless steel tubes to the side of the lid. These tubes allow gas to enter and leave the SAW device. After polymer coating is complete, the lids are glued to the headers with Devcon 5-minute Epoxy (Danvers, MA) to form a gas tight seal where the lid meets the header. Note that the glue used contained a polyamine, as opposed to a volatile amine which could leach out of the cured epoxy and affect the SAW device response.

2 SAW DEVICE COATING

2.a Selection Procedure

The choice of polymeric coatings for use with SAW chemical microsensors is an important factor in the development of a successful operating sensor system. In order to select a polymer coating for a particular analyte vapor the solubility properties of the polymer need to be tailored to the analyte vapor. This is not as simple as the old rule of thumb that "like dissolves like" especially if the analyte vapor(s) contain functional groups with significant hydrogen-bonding properties. In previous studies coating selection was determined by a time consuming method involving screening a large number of polymers and testing each one as a SAW coating for each vapor of interest. The initial selection of polymer coatings was largely based on personal experience with some chemical intuition. However more recently we have developed much more rigorous and scientifically based selection procedures. These methods employ a high level of understanding of the solution process that occurs when a vapor dissolves in a polymer. The affinity of a polymer coating for the analyte vapor of interest depends upon the solubility properties of both the polymer coating and the analyte vapor. The selection process for polymer coatings used in fire vapor detection, and a detailed description of the factors that govern the solution process of a gaseous molecule in a polymer, is included in Appendix A.

The main characteristics for suitable SAW device coatings are:

1. Strong coating affinity for analyte vapor of interest with high selectivity over possible interferents. (see Appendix A)

2. Reversible coating-vapor interaction by secondary forces such as hydrogen-bonding, dipolar, and van der Waal or London dispersion forces, with no covalent bond formation. (see Appendix A)
3. High permeability for fast vapor absorption and desorption processes. This normally requires polymer glass transition temperatures that are below the SAW device operating temperature.
4. No significant polymer volatility over a period of 12 months.
5. Good coating morphology properties, i.e. forms uniform thin film coatings without undesirable dewetting processes that can lead to polymer beading.

For fast vapor absorption, polymers with high permeability are required. The physical characteristics that normally accompany highly permeable polymers are low density with low crystallinity. Polymers with increasing "polar" properties are normally associated with larger contributions of crystallinity and do not make good candidates for SAW coatings because crystalline domains exhibit low permeation properties. This is unfortunate because "polar" properties of polymers are the characteristic that we want to take advantage of in designing selectivity into SAW device coatings. One way to significantly reduce the contribution of crystallinity is to raise the operating temperature of the polymer coated SAW device to higher than the glass transition temperature of the polymer T_G . At the glass transition temperature a polymer changes from a hard rigid glass (with crystalline properties) to a rubber-like state (without crystalline properties). The glass transition is accompanied by a large increase in segmental motion in the polymer chain which allows a pronounced increase in permeability. However raising the operating temperature in a SAW sensor system is

undesirable because at elevated temperatures interactions such as hydrogen-bonding become much less pronounced and selectivity is lost. In addition $\log K$ values are inversely related to absolute temperature, so that small increases in temperature will affect the partitioning of vapor into the polymer coating by a logarithmic factor leading to large losses in SAW device sensitivity.

Thus for high permeability properties SAW polymer coatings should have low T_G values which are less than the SAW device operating temperature. These properties are found in rubbery polymers.

In addition the polymer must be non-volatile, and if applied to the SAW device by spray coating it must be soluble in a volatile solvent and exhibit stable well-formed coatings on the surface of the SAW device. Polymer volatility is related to molecular weight and if volatility is significant it can often be eliminated by crosslinking chains together. However too much crosslinking is normally accompanied by a decrease in permeability and can make the polymer difficult to dissolve in a solvent. Polymer wetting properties are influenced by both the polymer functional groups in contact with the surface and the functional groups present at the surface to be coated. If wetting to the surface of a SAW device is poor, polymer beading is the likely result, and can lead to acoustic wave losses into the film that are so large that the SAW device fails to oscillate. In addition beading leads to areas of polymer that are relatively thick, which increases the length of time required for sorption processes to equilibrate and hence increases sensor response time. For poorly wetted polymers the surface of the SAW device can be modified by covalent attachment of organosilanes to improve the quality of poorly wetted coatings [19,20]. One class of polymers worthy of special mention is the family of polysiloxanes. These polymers exhibit some of the lowest polymer glass transition temperatures available, and can be readily synthesized with different pendent groups in the repeat unit, so that a series of polysiloxanes can be made with a

wide range of solubility properties. The only draw back appears to be their poor wetting properties sometimes indicated by polymer beading. However within the scope of plasma cleaning SAW devices to generate high energy surfaces and organosilane treatments, we can reproducibly coat these polymers as stable thin films.

2.b Polymer Selection Process Summary

The particular problem of detecting vapors given off from a variety of fire fuels provides a more complex challenge than has previously been tested. Normally a known analyte vapor has been the detection challenge mixed with 1 or 2 possible background interferents [1]. Mixtures of fire vapors are more complex and this makes the selection of SAW device coatings a more difficult process. In addition, normally not all decomposition products are known, and if they are then the information is limited and normally restricted to flaming fire data, which may not apply well to smoldering fire situations. From previous work [21-23] it is clear that a wide range of organic vapors are expected to be released from different fire fuels. In order to meet these challenges a 4 SAW device array was chosen with 4 different polymer coatings that can provide a wide range of solubility properties.

From the selection process based on solubility properties, described in Appendix A, the polymers considered as strong candidates for a 4 SAW array were: SXFA, SPYR, OV202, PECH, and PIB. SXFA is a polysiloxane material synthesized by the reaction of hexafluoroacetone with an allyl-substituted polysiloxane [17]; SPYR is an alkylaminopyridyl-substituted polysiloxane; OV202 is a poly(trifluoropropyl)methylsiloxane; PECH is poly(epichlorhydrin); and PIB is poly(isobutylene). From these 5 candidates OV202 was eliminated due to the volatile nature of the polymer sample and SPYR was removed from consideration because of its large responses to changes in ambient humidity, which could be confusing to

pattern recognition efforts. This is especially the case when the ambient gas sampling mode is used. To replace OV202, poly(ethylene maleate), PEM, was chosen as the fourth coating because it showed the largest dipolarity of all the polymers studied and did not respond greatly to water vapor even though the "a" coefficient which indicates polymer hydrogen-bond basicity was intermediate for the polymer coatings studied. The final coating selection was SXFA, PECH, PIB, and PEM; each provides different information about the vapors present. SXFA is a strong hydrogen-bond acid and hence provides information about hydrogen-bond basic vapors. PEM is strongly dipolar and hydrogen-bond basic, and therefore provides information about dipolar and hydrogen-bond acidic vapors. PIB interacts by van der Waal or dispersion interactions and is a good coating for hydrocarbon fuels. PECH combines a range of solubility properties including dipolar, hydrogen-bond basicity and acidity, and is a good coating for a wide range of vapors with different solubility properties.

2.c Coating Procedure

2.c.i SAW Device Finishing Techniques

Prior to polymer coating each SAW device was thoroughly cleaned by solvent rinsing, to remove soluble organics and plasma etching [24] to remove any residual contaminants. Cleaning SAW devices in a plasma provides a high energy surface to which polymers can easily adhere forming stable thin films [20].

2.c.i.(a) Solvent-Cleaning Method

As received, SAW devices were dip rinsed with chloroform, methanol and acetone. The pins of a SAW device are held in a clean pair of tweezers and the SAW device is plunged through the meniscus of the solvent several times. From noting the observed SAW frequency before and after solvent rinsing it is quite often observed to

shift to a higher value indicating that solvent rinsing has removed contaminating material.

2.c.i.(b) Plasma-Cleaning Method

After solvent cleaning the SAW devices were placed in a Harrick plasma cleaner. The chamber was evacuated until the pressure was approximately 100 millitorr and an air plasma (sky blue) developed by turning the r.f. power on. When the pressure within the plasma chamber was allowed to equilibrate prior to turning the plasma on and the plasma is ignited, the pressure within the chamber was observed to increase as the SAW devices were cleaned. We interpret this to be the volatilization of organic/inorganic material present on the surface of the SAW device as the cleaning procedure advanced. The return to the lowest pressure reading normally took no longer than 1 minute, but the plasma cleaning process was typically extended to between 15 to 20 minutes.

2.c.ii Polymer Spray-Coating

Polymer coating and laboratory vapor testing were as described before [25]. In brief, the polymer films were applied using an airbrush and a dilute solution of polymer in HPLC-grade chloroform; the frequency of the SAW was monitored in real time during the coating process. The frequency of the SAW was measured during coating and vapor testing using a Philips PM6674 Universal frequency counter with GPIB interface. The frequency versus time data were acquired and stored on an IBM-compatible PC equipped with a National Instruments AT-GPIB interface card running software developed at the Naval Research Laboratory. The frequency data were obtained to 1 Hz resolution.

All polymers tested coated the SAW devices uniformly. After examination under an optical microscope, the device lids were glued to the headers. The operating frequency of each device was monitored over a period of time and no significant loss in polymer coating was observed. The initial polymer coating thicknesses expressed in KHz are shown in Table 1, together with codes that locate the specific SAW device used. The two letter code, e.g. "CG", is engraved on the base of the SAW device to avoid later confusion.

Table 1 SAW device Spray Coating Results

Coating	Code	Coating Thickness/KHz	Coating Date	Mentor Channel#	Vapor Exposure Order
SXFA	CG	322	13Sep93	0	1
PEM	CF	300	13Sep93	1	4
PECH	CA	251	14Sep93	2	3
PIB	BY	290	10Aug93	3	2

3 GAS SAMPLING SYSTEM

Two main methods of sampling air were employed and these are referred to as the ambient and preconcentrator modes [1]. Ambient testing exposes the sensor array immediately and in the preconcentrator mode gas is collected over a period of time on an adsorbent column and periodically thermally desorbed to send a concentrated gas sample to the sensor array. Both methods were tested but the ambient mode proved to be the only one practically acceptable so the preconcentrator mode will not be dealt with further. All tubing and parts exposed to vapor upstream of the gas sampling pump were teflon or teflon coated. A teflon membrane filter assembly with a 20 μ m teflon

membrane from Berghof (Concord, CA) was used at the inlet to prefilter the sampled gas of any particulates. The general layout of the sensor system is shown in Fig 4.

3.a Ambient Sampling Mode

Two configurations were employed in this mode and they are illustrated in Fig 5. The configuration in Fig 5a is the normal configuration and all results presented in this report refer to data collected in this mode. In Fig 5b a charcoal scrubbing column can be accessed by actuating a valve. This allows the air being sampled to be cleaned of organic vapors and provides clean air for baseline information of the SAW sensor array. The use of a charcoal scrubbing column provides the means to purge the sensor array and reset the baseline of the instrument and can be programmed to occur at timed intervals. This is a useful procedure if the air being sampled is normally from a "clean" atmosphere. However, if the air normally contains a significant contribution from hydrocarbon vapors, a baseline will be established when the SAW array samples ambient air that corresponds to this "normal" level of hydrocarbon vapors. This situation might be a common one on board a ship environment, for example in the engineering compartment below deck. A release of organic vapors from a fire threat would give rise to signals in excess of the already established baseline and would be detected, and the source material identified. The use of a scrubbing column in this situation would provide misleading results because it would not provide true baseline information for the air being sampled; this could result in the sensor system not correctly identifying the fire threat.

The fire chamber used in these studies was contaminated from tests conducted prior to our use, and a layer of soot lined the walls. When the sensor array sampled the air from the fire chamber a new baseline was established reflecting the level of contamination from old experiments. After observing this problem the fire chamber

was cleaned down to the original paint, which reduced these effects significantly, but the fire chamber always gave rise to some response from residual contamination. Running the experiments in a chamber that already had significant levels of hydrocarbon vapors did not impact on the overall results but did make the experiments more difficult to set up, in terms of the length of time required to allow for baseline equilibration.

3.b Four SAW Sensor Array

An important aspect in the operation of chemical sensor systems is the time taken to respond to vapor once exposed. In SAW sensor systems this is related to the sampling system configuration and primarily includes the dead volume generated by tubing and the flow rate developed by the pump. In addition, when the polymer coating is exposed to vapor there is a finite time taken for vapor to absorb into the coating. This is related to the coating thickness, the permeability of the polymer at the operating temperature, and to the size of the vapor molecules being tested.

Optimization of the gas sampling systems requires design of tubing configuration that minimizes dead volume. The flow rate can be increased by using a larger pump, but there is no advantage in excessive pumping rates because at some point some other process will become the rate determining factor for sensor response time, and larger pumps require more power to operate and are accompanied by higher noise levels.

The 4 SAW sensor array was connected in series and the order of polymer coating exposure was SXFA, PIB, PECH, and PEM last. A series connection minimizes pumping requirements and tubing arrangement, but has the slight disadvantage of incremental dead volume which was not significant when compared to the tubing volume and the pumping rate of about 200 ml/min.

4 MATERIALS

Four possible shipboard materials were tested under smoldering conditions and 2 common shipboard liquids were tested at chamber temperature.

4.a Polyimide

Polyimide thermal insulation foam samples were provided by NRL Code 6180 (ca. 8x5x $\frac{3}{8}$ in, 10g). The polyimide foam was a development product manufactured by Imitec, Inc. and used in Phase1 of the Submarine R & D Hull insulation program.

4.b Fiber Glass

Fiber glass thermal insulation samples (ca. 8x5x $\frac{3}{8}$ in, 40g) were provided by NRL Code 6180. The bulk of the fiberglass was similar to that used in household insulation but the front exposed to heat was a woven fiberglass fabric. The fiberglass was a development product manufactured by Manville and used in Phase1 of the Submarine R & D Hull insulation program.

4.c Coaxial Cable

Coaxial cable samples (0.5in in diameter) were provided by NRL Code 6180. The coax cable was manufactured by Teledyne Thermatics, and the Military specification number is M17/29-RG59 MIL-C-17 12515.

4.d Absorbent Cotton

Absorbent Cotton (purified cotton U.S.P sterile) was obtained from Parke-Davis #30-716-55. Samples were cut to 5x5x $\frac{3}{8}$ in.

4.e AFFF Fire Fighting Solution

AFFF fire fighting solution was provided by NRL Code 6180. The AFFF was a 6% solution manufactured by 3M (St. Paul MN), batch number 165, date of mfg. 12/90, sampled from 55 gal. drum at NRL Chesapeake Bay Detachment (CBD). The 6% solution is a concentrated solution that is diluted with 94 parts water to 6 parts AFFF when used to fight a fire. For the purposes of a spill or leak detection the AFFF was used in the concentrated form.

Table 2 3M AFFF FC-206CE approximate composition

Component	% by weight
Water	76.0
2-(2-butoxyethoxy)ethanol	15.0
Urea	4.0
Fluoroalkyl Surfactants (e.g. perfluorooctyl sulphoamide-N-propyltrimethyl ammonium iodide)	<5.0
Synthetic detergent	<5.0
1-methyl-Benzotriazole	<0.1

The 3M product information sheet gives the approximate composition by weight shown in Table 2. Foams of 6% AFFF cover hydrocarbon liquid-based fires and extinguish them by oxygen starvation. The component most likely to be detected by the SAW sensor system is 2-(2-butoxyethoxy)ethanol. This component is used as a refractive index modifier and helps make the AFFF visible to the operator.

4.f Hydraulic fluid

Hydraulic fluid was obtained from Stauffer Chemical Co. (Westport, CT) the trade name for this product is Fyrquel EHC. The hydraulic fluid is described as fire resistant and contains trixylenylphosphate.

4.g Polymer and Solvent Materials

PIB was obtained from Aldrich (Cat. No. 18,145-5); PECH was obtained from Aldrich (Cat No. 18,186-2); PEM was provided by Art Snow (NRL 6120) and is the same material used in past chemical sensor investigations [9]. SXFA was synthesized according to the method described in reference [17] but modified to yield a higher MW polymer. SPYR, was provided by Martel Zeldin and William Fife at Indiana-Perdue University at Indianapolis. OV202 was obtained from Phase Separations Limited. The liquid organic solvents used to generate vapor streams were commercial chemicals of 99% or greater purity, except nitromethane (Fisher certified ACS, Assay 95.4%). Chloroform used for preparing solutions of polymers was obtained from Aldrich and was HPLC grade (Cat. No. 27,063-6). These reagents were used as received. The water used was triply distilled, with the last two distillations in an all-quartz still.

5 SMOLDERING FIRE TESTS

The fire tests described in this report were all conducted in a 177ft³ fire chamber situated at NRL.CBD. The fire chamber is located inside a building that was temperature regulated to approximately 22°C with an air conditioner unit. The interior of the fire chamber is accessible by a door which is large enough to allow entry into the fire chamber, which is about large enough to stand up in. The interior walls are made from steel and had been painted. Two glass portholes allowed experiments to be viewed from outside and holes with swagelok fittings provided access inside the chamber for electrical cables or tubing that were necessary. The fire chamber was equipped with two circulating fans and a venting line that allowed vapors and smoke to be vented outside the building by blowing air into the chamber through an open

valve and out the vent. With the door shut and chamber valves closed the interior can be pressurized but in the experiments described all tests were conducted at atmospheric pressure.

The samples were clamped to a wire gauze or in the case of coax cable, paper clips were used to hold a lattice of cable to the wire gauze (refer to Fig 6 for experimental set up). This was held securely in a metal stand positioned in front of a pyro-panel Model 4083-5-6 consisting of 4 quartz lamps, from Research Inc, (Minneapolis, MN). The pyro-panel was also held in place by a metal stand and the distance from the quartz lamps surfaces to the front of the test material was varied from 2.5-3.5 inches depending on the sample under test. The two metal stands with test material and pyro-panel were positioned centrally toward one end of the fire chamber and in view of the left porthole. The SAW sensor system was positioned at the other end of the chamber on the grated metal floor. This corresponded to about 1.5ft lower than the pyro-panel, and the distance from the gas sampling inlet to the test material was about 5ft. A serial cable was connected to the serial port of the SAW sensor system and the other end was connected to a host computer outside the fire chamber. This allowed each of the 4 SAW devices in the array to be monitored. The SAW responses are plotted in a frequency versus time plot in real time, and other additional information about the experiment is included. A typical screen display is shown in Fig 7. The SAW sensor system was turned on and the ambient sampling mode selected. After all the test equipment was set up, the fire chamber door, vents and valves were closed off.

A period of time was allowed for equilibration between residual vapors in the fire chamber and the sensor array, and for the sensor array to reach the setpoint temperature of 25.0°C. The peltier cooling/heating control took about 15 minutes to bring the temperature of the sensor array to 25.0°C, but the time required to allow

equilibration of the sensor array with residual vapors was of the order of 1-2 hours. All 4 sensors responded to this background level of residual vapor and the slow rise in signal frequency eventually leveled out at some new baseline level. If not enough time is allowed for the baseline to level out the slight drift during a fire experiment can be corrected for. The reason for the long equilibration time was not clear but may be due to the size of the vapor molecules being detected. The larger the molecules the slower is vapor diffusion into the polymer coatings. For molecules with molecular weights of less than about 100, the time lag for diffusion is negligible. As the molecular weight increases diffusion may become increasingly significant as a factor in determining sensor response time. Note that the polymer coatings are very thin (estimated at between 30-50 molecular layers thick assuming uniformity) so vapor equilibration is expected to be rapid. In laboratory and field tests we have not observed long drift problems and studies are under way to investigate the effect more closely.

After baseline equilibration the power supply to the pyro-panel was adjusted (0-100V) so that the radiant heat flux was sufficient to just cause faint traces of smoke from the test sample. At this point the power to the pyro-panel was immediately reduced to a voltage where smoke production ceased. For some test materials once the heat necessary for the onset of smoke was reached it was difficult to stop all smoke production, as was the case for cotton and coax cable. Cotton was particularly troublesome and if care was not taken it could spontaneously ignite. However in all cases smoke production was limited, unless deliberately forced.

When sufficient data had been collected during vapor generation the pyro-panel was turned off, and normally the sensor system was allowed to continue sampling the gas for a period of time before venting the fire chamber. The fire chamber was vented by opening two valves, one opening the vent line and the other leading to a fan designed to push air from the laboratory into the fire chamber and

through the venting line to outside the building containing the fire chamber. This venting procedure was not very efficient due to tubing restriction preventing a sufficient purge rate. Purging under these conditions took several hours and was normally performed overnight. Opening the door to the fire chamber greatly enhanced purge rates but because of the possible toxic nature of the vapors evolved this was not normally an option.

6 LIQUID SPILL SIMULATION TESTS

The experimental set up was as described above in the smoldering fire tests except the vapors were generated by sitting a bath of the liquid in the 177ft³ fire chamber. A polyethylene container (14x10x7in) was used with the liquid of interest to a depth of ca. 1in and was located ca. 5ft from the SAW sensor system. After the SAW sensor system had temperature equilibrated to 25.0°C and the baseline was steady, the door to the fire chamber was opened and the bath of liquid was placed inside and the door closed. The time taken for this operation was approximately 15s. After sufficient time had been allowed to collect vapor exposure data the door was opened and the bath of liquid removed to a remote location. The fire chamber was allowed to vent unassisted into the laboratory with the door open. The decontamination of the fire chamber was followed until the SAW signals had returned close to the original baseline level and the door was then closed.

7 DATA ACQUISITION & PATTERN RECOGNITION

The microcontroller is equipped with a serial port which is used to output data to a host computer during system development and testing. Mentor, a user "friendly" software program, was developed in-house at NRL to plot these data in real time and carry out pattern recognition when vapors are detected. Mentor 2.0 is a Windows-based application created using the Visual Basic 2.0 programming environment and is described in Appendix B. A 12ft cable was used to communicate with and transmit data from the SAW sensor system situated inside the fire chamber and an IBM compatible computer situated outside the fire chamber (see Fig 7). Alternatively data could be logged to a Macintosh computer using Smartcom II, without real-time plotting capabilities.

RESULTS AND DISCUSSION

1 Smoldering Fire Tests

Several test configurations were employed with different sampling systems and temperature control. Two fire chambers were used; "FIRE 1" chamber (10,000ft³) and the smaller 177ft³ fire chamber. The two types of vapor sampling systems tested were in the preconcentrator or ambient modes described earlier. Experiments performed in the FIRE1 chamber were for flaming diesel and heptane fires. No reliable data was collected from FIRE1 tests, primarily because at this stage of the system development the temperature control of the sensors was inadequate, and also the sampling system to the sensor system outside the chamber used a long stainless steel tube (ca. 30ft) which was contaminated from previous experiments. The decision to move the fire tests to a smaller 177ft³ fire chamber was to provide more flexibility. Because the

SAW fire tests were the only experiments scheduled in the fire chamber, there were less complications in planning tests and there was no chamber contamination with other ongoing experiments.

Initial experiments in the 177ft³ fire chamber were conducted with the sensor system situated outside of the fire chamber and connected via a clean stainless steel (SS) tube to the interior of the fire chamber. A wire gauze filter attached to the end of the SS tube was situated directly above the smoldering fire for vapor sampling. With the vapor sampling in the preconcentrator mode (2 minute cycle) smoldering fire data was collected for polyimide insulation foam, Mil C17 Coax cable and plastic backed fiber glass insulation. Unfortunately the SAW device responses after thermal desorption of collected vapors was very slow to return to baseline and for repeated preconcentrator cycling gave rise to a stepwise increase in the apparent baseline from each sensor. The sensors appeared to be responding to vapor and not particulates because the gas is filtered prior to being collected on tenax material in the preconcentrator column. The reason for the slow recovery time was not clear, and was a major concern because the sensor system is intended as a reusable analytical instrument. To investigate further a glass wool plug was placed at the gas sampling port of the SAW sensor system, and after smoldering fire tests no particulates were observed. It was concluded that the vapors generated under smoldering conditions contain large, relatively non-volatile molecules at the SAW device operating temperature but volatile under thermal desorption.

After the preconcentrator mode experiments, the ambient sampling mode was favored and a 20 µm teflon membrane used to filter the sampled gas. In addition the SAW sensor system was placed inside the fire chamber so that no tube external to the sensor system was necessary. The 20 µm teflon membrane served to keep out any smoke particulates but also proved to be beneficial in preventing large molecules from entering the sampling system. The system set up in this configuration gave rise to

reversible responses on all sensors but in some instances these were slower than desired. In future tests a 10 μm teflon membrane filter would further limit the exposure of the sensor array to relatively large molecule vapors.

Some of the experimental parameters that describe and characterize the smoldering fire experiments are shown below in Table 3. The 4 SAW array patterns generated by the different fire fuel and liquid spill tests are compared in Fig 8. Significant events during the fire tests or simulated liquid spills are indicated on the frequency versus time plots for each fuel in Figs 9-14. Note that each material tested has a unique signature SAW sensor array pattern. For each of the fire fuels, all 4 sensors responded significantly, whereas the sensor responses for the liquids showed marked responses for some polymer coated devices and weak responses in others. The hydraulic fluid tested in the configuration used in these experiments gave little or no response on any of the 4 SAW sensor array.

1.a Fiber Glass

An examination of the fiber glass before and after exposure to the pyro-panel showed that the white woven fiber glass cover had been scorched to a light brown. The more fibrous material below this was also discolored but not by as much, and to a depth of about 1/8in. The vapors released by thermal decomposition gave responses on all 4 SAW devices (refer to Fig 9a), the largest response was shown with the PIB coating and the next strongest response was for the SXFA coating. Sensor responses (difference frequency) all increased at similar rates although further into the experiment at about 2100s PIB and SXFA did increase more rapidly while PECH and PEM rose at steady rates.

Table 3

Smoldering Fire Results in 177ft³ Fire Chamber

Fire Fuel	Polyimide	Coaxial Cable	Fiber-glass	Cotton
File Name	dfoam	bcbl	bfgl	bcott
Experiment date	Sep93	24Sep93	28Sep93	27Sep93
Gas Sampling Configuration	Ambient	Ambient	Ambient	Ambient
Fire Chamber Volume	177ft ³	177ft ³	177ft ³	177ft ³
Sample-Quartz Lamp distance/in	2.5	3.5	2.5	3.5
Initial Weight ^a /g	10.72	117.01	39.44	11.91
Final weight ^a /g	10.66	116.98	39.34	11.55
Weight loss/g	0.06	0.03	0.10	0.36
SAW array/ ^o C T min-max	25.0-25.2	25.1-25.2	25.0-25.3	25.1-25.3
T/ ^o C 177ft ³ Chamber Initial	22.0	22.6	23.4	22.2
T/ ^o C 177ft ³ Chamber Final	--	--	24.3	--
RH % 177ft ³ Chamber Initial	56.1	45.4	52.4	48.6
RH % 177ft ³ Chamber Final ^b	--	43.0	--	48.7
Heat Lamp Voltage/V min-max	60-70	50-70	40-70	45-65
Flow rate at Inlet/mlmin ⁻¹	200	200	220	200
20 μm PTFE Membrane filter	Yes	Yes	Yes	Yes
Circulating Fan	Yes	Yes	Yes	Yes

a: Sample weights were measured in a draft free enclosure and the sample was allowed to equilibrate to the ambient laboratory humidity for 30minutes before taking a reading.

b: Prior to venting fire chamber

The radiant heat panel was turned on at 1768s and within 40s the first significant responses were indicated by a rise in sensor oscillation frequency. The initial response time is a function of the distance between the sample being heated (5 feet) and the air currents that distribute vapor. Another major factor is the concentration of vapor produced, and by how much it is diluted. In this experiment the vapor is diluted by a circulating fan in 177ft³ of air and the heating rates were gentle enough to avoid smoke production. If the heat generated by the pyro-panel was sufficient to momentarily generate smoke, the power was immediately reduced to below this level. The sensor response time is expected to be less for higher levels of heat flux, because thermal decomposition would occur more rapidly with larger releases of vapor. Larger releases of vapor would allow the sensors to detect the vapor more rapidly because threshold levels of detection would be reached in a shorter period of time.

A visual snapshot of the array patterns produced at 200 s time intervals is shown in Fig.9b. After switching on the pyro-panel the 4 SAW array generates signals which develop to a constant pattern.

1.b Polyimide Foam

An examination of the yellow foam before and after exposure to the pyro-panel showed that the polyimide had been discolored by heating to a light brown color. This discoloration extended below the surface to about 0.25in, and was more intense below the surface in the bulk of the foam. In addition the piece of foam shrunk in the middle of the sample where the heat fluxes were highest. The shrinkage produced a concave structure, the depth of which was about 3/8in at the shallowest point. This

resulted in an increase in the distance between the sample and heat source. In order to adjust for this effect the heat flux was increased during the experiment by raising the applied voltage to the pyro-panel. The vapors released by thermal decomposition gave responses on all 4 SAW devices (refer to Fig 10a), the largest response was shown with the SXFA coating and the next strongest response was for the PEM coating, indicating that some component of the mixture of vapors is dipolar and hydrogen-bond basic. The apparent meandering in response shown for PIB and PECH coated SAW devices is due to the operator manually adjusting the SAW array temperature to counter for a temperature drift problem. It is interesting to note that the SXFA and PEM were largely unaffected by this slight temperature adjustment (0.2°C). Taking into account the variations due to temperature adjustment, the sensor responses (difference frequency) all increased at similar rates indicating that the array pattern of responses will be similar at different stages of the experiment (Fig 10b).

The radiant heat panel was turned on at 2368s and within 20s the first responses were indicated by a rise in sensor oscillation frequency. When the venting fan was turned on all sensor signals started to drop but after a short time they started to rise again. When the door to the fire chamber was opened, venting was more efficient and all sensors started to drop towards the original baselines. The rise in sensor signals shortly after venting was initiated is probably due to a temporary rise in vapor concentration as a result of increased air flow within the fire chamber, releasing vapor adsorbed to the walls of the chamber. This can be likened to the increased release of water vapor from clothes drying in ambient air, which is enhanced when the wind is blowing.

A visual snapshot of the array patterns produced at 200s time intervals is shown in Fig.10b. After switching on the pyro-panel the 4 SAW array generates signals which

develop to a constant pattern. The first couple of patterns do change, but this is largely due to the temperature fluctuation discussed earlier.

1.c Coaxial Cable

An examination of the cable before and after exposure to the pyro-panel showed that the black plastic sheathing was largely unaffected by the heat applied, however at the highest heat flux, in the center of the sample, the black matt appearance of the cable had been replaced by a glossy surface. The pyro-panel was turned on at 3980s and within 30s the first significant responses were indicated by a rise in sensor oscillation frequency. The vapors released by thermal decomposition gave significant responses on all 4 SAW devices (refer to Fig 11a), the largest response was shown with the SXFA coating and the next strongest response was for the PIB coating. The sensor responses (difference frequency) for PIB, PECH and PEM all increased at similar rates indicating that the array pattern of responses for these coatings will be similar at different stages of the experiment. For the SXFA coating the response profile is somewhat different and responds slowly at first to vapors released by coax cable but then rises more rapidly than the other coated SAW devices. This may be due to the release of different vapors as the "smoldering fire" develops. As a result the SXFA frequency versus time plot crosses over the other frequency-time response lines at about 4200s, but beyond about 4400s the SXFA responses mirror those of the other coated SAW devices. At 4800s the pyro-panel was turned off, and the SAW responses all leveled out, because no further vapor is generated and the chamber is sealed so that vapors cannot escape until venting the fire chamber.

The coax cable was more prone to generating smoke than the foam or fiberglass and once smoke was generated it was more difficult to stop without a large

reduction in power to the pyro-panel. However after repeating the tests several times the heat was controlled to minimize any smoke.

A visual snapshot of the array patterns produced at 100s time intervals is shown in Fig. 11b. After switching on the pyro-panel the 4 SAW array generates signals which develop to a relatively constant pattern. The signal on the SXFA coated device is slower to develop as indicated earlier.

1.d Absorbent Cotton

An examination of the cotton sample before and after exposure to the pyro-panel showed that the white appearance had become discolored to a light brown and charred to black at the center of the sample exposed to greatest heat. The pyro-panel was turned on at 1170s and within 30s the first significant responses were indicated by a rise in sensor oscillation frequency. The vapors released by thermal decomposition gave significant responses on all 4 SAW devices (refer to Fig 12a), the largest response was shown with the PEM coating and the next strongest response was for the SXFA coating. The sensor responses (difference frequency) for all 4 polymer coatings increased at similar rates indicating that the pattern of responses for the array will be similar at different stages of the experiment.

The cotton was the most difficult of all the samples tested to control the heat applied without generating smoke, and in some earlier experiments the cotton erupted into flame. The heat was controlled to minimize any smoke initially, and at 1710s the heat applied was increased to deliberately produce smoke. This is indicated by a sharp deviation in the slope of the frequency-time lines for all 4 polymer coatings, and reflects the increased rate of vapor release. It is interesting to note that relative slopes

of the response lines remain nearly constant before and after smoke generation. At 2710s the pyro-panel was turned off and the SAW responses leveled out. At 3170s the venting fan was turned on and all sensor responses started to drop towards the original baselines.

A visual snapshot of the array patterns produced at 200s time intervals is shown in Fig. 12b. After switching on the pyro-panel the 4 SAW array generates signals which develop to a constant pattern until venting the fire chamber.

2 Simulated Liquid Spills

2.a AFFF Fire Fighting Solution

The vapors released at the chamber temperature (23.4°C) from a bath of AFFF gave a strong response with the SXFA coated device and moderate with the PEM coated device, the other two sensors gave weak signals (refer to Fig 13a). It seems clear that the SXFA coated sensor is responding to the refractive index modifier 2-(2-butoxyethoxy)-ethanol. The sensor responses (difference frequency) for all 4 polymer coatings increased at similar rates indicating that the pattern of responses for the array will be similar at different stages of the experiment. The SAW noise level in this experiment is higher than in previous tests and the reason for this is not clear. It was not related to any sensor array temperature drift because this was closely monitored and the temperature changed by only $\pm 0.05^\circ\text{C}$ during data collection.

The AFFF bath was placed in the fire chamber at 2164s and within 30s significant SAW responses were indicated. These signals rose as the vapors from the AFFF equilibrated within the fire chamber, and this can be followed by the curved SAW responses. To vent the chamber the AFFF trough was first removed and the chamber

door left open at 3064s, the sensor signals immediately started to drop towards the original baselines. Note, this is not the forced venting that was used in the smoldering fire tests.

A visual snapshot of the array patterns produced at 200s time intervals is shown in Fig. 13b. After exposure to AFFF the 4 SAW array generates signals which develop to a constant pattern until venting the fire chamber.

2.b Hydraulic Fluid

The vapors released at room temperature from a bath of hydraulic fluid gave no detectable responses on any of the 4 polymer coated SAW devices (Figs 14a,b)

3 Pattern Recognition

A neural network routine trained with over 500 patterns from fire vapor tests correctly identified the source material for all fire threats and distinguished them from possible interferents (e.g. AFFF and hydraulic fluid).

CONCLUSIONS AND RECOMMENDATIONS

The SAW sensor system used in this study performed exceptionally well and the SAW devices were not adversely affected by the filtered smoke developed from smoldering fires. A neural network routine trained with over 500 patterns from fire vapor tests correctly identified the source material for all fire threats tested and distinguished them from possible interferences. The 4 SAW array patterns generated from the test materials used produced unique patterns for each material (Fig 8). These tests covered only a small fraction of the possible materials that can fuel fires and are present onboard a ship. It is clear that a more comprehensive list of test materials will have to be studied as part of a larger effort. When a larger database of materials is tested, it is possible that some patterns generated may be too similar to distinguish between. For example, different types of electrical cabling may generate very similar patterns, in which case these materials could be grouped together as a general class of material. Alternatively the selectivity of the SAW sensor system could be enhanced by increasing the size of the sensor array from 4 to 6 SAW devices. The present system is compatible with handling signals from a 6 SAW sensor array and the increase in array size would not affect the implementation of the neural net pattern recognition software.

Two main types of gas sampling were tested and the one preferred by far was the ambient mode, in which the sensor array samples the ambient gas immediately and continuously. In the preconcentrator mode, vapor collected and concentrated on an adsorbent column and thermally desorbed periodically gives rise to signals every 2 minutes, and greatly increases the sensitivity. For the purposes of fire detection valuable time would be lost and sensitivity does not appear to be a problem for the materials tested. SAW frequencies are monitored every 2 seconds in the ambient

mode, but this data sampling time could be reduced to decrease detection time or increased to reduce data handling.

One area of concern with the present hardware is the SAW device temperature control, which was found on occasion to be not as precise as required. Any temperature variation in the sensor array leads to SAW device baseline drift which in turn affects the threshold limits that are set for vapor detection. From results of these tests we have implemented some modifications and planned others to improve temperature control so that the temperature variation over a 60 minute period is no more than $\pm 0.1\text{C}$. The improvements could include a more sophisticated engineering design of the temperature control electronics board and the design of the housing that encloses the SAW device array, which include a cooling fan and thermal insulation to aid temperature stability.

The fire tests performed in this work were under conditions of no smoke generation or mild smoldering smoke conditions; the SAW devices were not adversely affected under these conditions. Future work must include tests under all stages of fires from smoldering to flaming fires. Under these different fire conditions we expect that SAW sensor array responses will change and different patterns may be generated. The ultimate goal is to identify the material responsible for a fire and the stage (e.g. smoldering or flaming) of fire development.

SUMMARY

A SAW sensor system has been demonstrated as a reliable sensor technology for fire detection. SAW sensor systems have the potential to give an early warning prior to a flaming fire and, unlike a conventional fire detector in heavy smoke, identify the primary source material in the fire. This information will greatly assist in determining appropriate steps to take in preventing a flaming fire developing from smoldering material, and in taking the proper action in fighting flaming fires. In addition, the SAW sensor system can be used as a multitasking detector employing several pattern recognition algorithms to analyze simultaneously for vapors associated with fires or potential fires, and hazardous chemical vapors from spills, leaks or chemical agent attack. Because the sensor responses are reversible, an area exposed to toxic fumes can be monitored in real time as a decontaminating procedure progresses to a safe condition for personnel to enter the area. SAW sensor systems could ultimately be integrated into the shipboard damage control system using a serial communications port included in the present prototype. Processing of the sensor data could be done within each sensor system, relaying the results over the network, or the raw data could be sent over the network and processed at a central location.

The advantages of the SAW sensor system are:

- ◆ Fast response time (seconds) with high Sensitivity (down to pptr)
- ◆ Adaptability (fire vapors, chemical agent, toxic liquid spills)
- ◆ Multifunctional (detect vapors & mixtures simultaneously in real time)
- ◆ Electronics can be easily adapted for communicating information to a control center for continuous monitoring in real time and immediate action
- ◆ High tolerance of Interferent vapors
- ◆ Pattern Recognition techniques
- ◆ Rugged system (demonstrated in field tests including altitude tests in an Air Force cargo plane.
- ◆ Quantitative (response is proportional to vapor concentration).
- ◆ Longevity/durability (years)
- ◆ Few moving parts
- ◆ Power by 120VAC supply or a 12V battery.

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APPENDIX A

POLYMER SOLUBILITY PROPERTIES AND SELECTION

The solution process of a gaseous molecule can be described by two main processes which occur simultaneously but can be modelled separately.

Cavity formation: The first step involves the formation of a cavity in the solvent (the solvent in this instance is a thin polymer film) to accommodate a solute molecule. Cavity formation is an endothermic process and involves the separation of solvent molecules which requires energy to break any solvent-solvent interactions.

Insertion of solute molecule in cavity: Once the cavity is formed a solute molecule is inserted in the cavity and interacts with the surrounding solvent molecules. The solvent molecules may rearrange their dipoles and/or functional groups that can interact with the solute vapor molecule, in order to maximize their interaction while minimizing the loss of favorable solvent-solvent interactions. The solvent-solute (polymer-vapor) interactions include van der Waal or London Dispersion forces and when possible dipolar, polarizable and hydrogen-bonding interactions. All these interactions are exothermic and the balance with endothermic cavity formation largely decides whether a gas or vapor will dissolve in a solvent or polymer coating.

A new solvation equation has been developed to describe and quantify these various interactions and is given by the linear solvation energy relationship (LSER):

$$\text{Log } K = c + r.R_2 + s.\pi_2^H + a.\alpha_2^H + b.\beta_2^H + l.\text{Log } L^{16} \quad (3)$$

where log K is the log of the gas-polymer partition coefficient, K, and relates to a series of vapors for one solvent or polymer. K measures the strength of solute-solvent

interactions and for larger K values the solute is more soluble in the solvent. The explanatory variables are solute vapor parameters, R_2 an excess molar refraction, π_2^H the dipolarity, α_2^H and β_2^H , the hydrogen-bond acidity and basicity, and $\text{Log } L^{16}$ where L^{16} is the gas-liquid partition coefficient on n-hexadecane. The coefficients resulting from a regression of $\log K$ values characterize the solubility properties of the polymer, the most important being, "s" the dipolarity, "a" the hydrogen-bond basicity, "b" the hydrogen-bond acidity, and "l" a constant that reflects a combination of solvation cavity effects and dispersion interactions. The coefficient "r" reflects the polarizability properties of a polymer, and "c" is a constant resulting from the regression.

K values at infinite dilution are most easily determined by gas-liquid chromatography (GLC) with the polymer of interest acting as the stationary phase and these values are found to correlate with K values determined with a SAW device through equation 2. This is important because we can interpret K values determined by GLC rather than K values determined by SAW measurements which are more difficult to determine and interpret. Fourteen polymers of direct interest as SAW coatings have been characterized using values of $\text{Log } K$ determined by GLC in equation 3 [17,12]. The coefficients of the regression which characterize the solubility properties of the polymer are given in Table 4

The selection of polymer coatings for SAW chemical microsensors can now be made based upon the relative magnitude of "r", "s", "a", "b" and "l", and the solubility properties of the vapor of interest or possible background interferents. In addition this methodology allows the polymer selection process to be made for a new vapor challenge before any SAW measurements are made. When experimental $\log K$ values

Table 4 LSER REGRESSION COEFFICIENTS FOR POLYMERS AT 298K

POLYMER	CONSTANT c	POLARIZ- ABILITY r	POLARITY s	H-BOND BASICITY a	H-BOND ACIDITY b	DISPERSION CAVITY l	STATISTICAL INFORMATION n r sd
PIB	-0.77	-0.08	0.37	0.18		1.02	36 0.9959 0.073
SXPHB	-0.85	0.18	1.29	0.56	0.44	0.89	40 0.9943 0.089
PEM	-1.65	-1.03	2.75	4.23		0.87	31 0.9787 0.201
SXCN	-1.63	0.00	2.28	3.03	0.52	0.77	52 0.9916 0.150
PVTD	-0.59	-0.02	0.74	2.44	0.22	0.92	42 0.9951 0.073
PECH	-0.75	0.10	1.63	1.45	0.71	0.83	50 0.9964 0.068
PVPR	-0.57	0.67	0.83	2.25	1.03	0.72	33 0.9958 0.081
OV202	-0.39	-0.48	1.30	0.44	0.71	0.81	50 0.9967 0.071
P4V	-1.33	-1.54	2.49	1.51	5.88	0.90	26 0.9610 0.342
SXFA	-0.08	-0.42	0.60	0.70	4.25	0.72	36 0.9885 0.119
FPOL	-1.21	-0.67	1.45	1.49	4.09	0.81	26 0.9887 0.151
ZDOL	-0.49	-0.75	0.61	1.44	3.67	0.71	46 0.9952 0.086
PEI	-1.60	0.50	1.52	7.02		0.77	51 0.9873 0.151
SPYR	-1.94	-0.19	2.43	6.78		1.02	39 0.9886 0.120

are not experimentally available they can be easily predicted through equation 3 to an accuracy of about 0.1Log unit.

To illustrate this, LogK's using the solvent polymer phase, SXFA (polysiloxane with hexafluorocarbonyl pendant group) are calculated for solute vapors, dimethylacetamide (DMAC) and n-octane. The full LSER equation for SXFA at 298K is given below and the process of calculating LogK values for DMAC and n-octane is illustrated in Table 5. In addition to providing logK values a term by term investigation of the LSER equation indicates quantitatively the various contributions to the solution process. Such analyses help enormously in understanding the process of vapor sorption into polymer films used on SAW devices.

$$\text{Log } K_{\text{SXFA}}^{298\text{K}} = -0.08 - 0.42R_2 + 0.60 \pi_2^H + 0.70\alpha_2^H + 4.25\beta_2^H + 0.72\text{Log } L16 \quad (4)$$

Table 5 Log K calculation for DMAC and n-octane in SXFA at 298K

	Solute Parameter	DMAC	n-Octane
Polarizability	R_2	0.37	0.00
Dipolarity	π_2^H	1.33	0.00
Hydrogen-bond acidity	α_2^H	0.00	0.00
Hydrogen-bond basicity	β_2^H	0.73	0.00
Cavity+Dispersion	Log L16	3.717	3.677

LSER term	SXFA LogK term	LogK ^{DMAC} _{contribution}	LogK ^{Octane} _{contribution}
r.R ₂	-0.42.R ₂	-0.15	0.00
s. π_2^H	0.60. π_2^H	0.80	0.00
a. α_2^H	0.70. α_2^H	0.00	0.00
b. β_2^H	4.25. β_2^H	3.10	0.00
l. Log L16	0.72. Log L16	2.68	2.65
c	-0.08	-0.08	-0.08
	LogK ^{298K}	6.35	2.57

The calculated LogK values are $6.35(\pm 0.12)$ for DMAC and $2.57(\pm 0.12)$ for Octane. This means that for equivalent vapor concentrations DMAC will partition into the SXFA polymer coating much more strongly than the octane and be selectively detected by the SAW device. In fact for every one molecule of octane absorbed in the polymer coating approximately 6,000 molecules of DMAC will be reversibly absorbed for SAW sensor detection.

Polymer coating selection process based on LSER results. When interpreting the polymer solubility properties, "r", "s", "a", "b" and "l" there are two main criteria by which polymer coatings are chosen:

- 1 The magnitude of "c", "r", "s", "a", "b" and "l" should be considered first as this is related to the expected sensitivity and selectivity of a SAW coated device.
- 2 The relative magnitude of "r", "s", "a", "b" and "l" is also a very useful guide for coating selection because it indicates the coating selectivity. In particular the ratios of b/a , b/s , s/a and $l/(s+a+b)$ are very useful.

There are 5 solvent (or polymer) parameters in equation 3 we can vary, so theoretically if each of these parameters behaved orthogonally to each other there exist $5!$ or 120 combinations of different solubility properties possible. Unfortunately, in reality many of these combinations are not available, so for example it is not possible for a solvent molecule to exhibit hydrogen-bond basic or acidic properties without an associated dipolarity. However for such combinations where one solubility property is always partner to one or more other solubility properties we can choose to maximize one solubility property of interest while minimizing the other(s). Some of the more important combinations considered are described below and detailed in Table 6.

Table 6 Polymer solubility selectivity examined by ratios of LSERa Coefficients

POLYMER	h-b acidity/ h-b basicity b/a	h-b acidity/ dipolarity b/s	h-b basicity/ dipolarity a/s	dipolarity/ h-b basicity s/a	Σ "polar" interactions b+a+s	Dispersion/ Σ "polar" I/(b+a+s)
PIB	0.00	0.00	0.49	2.06	0.55	1.86
SXPFB	0.79	0.34	0.43	2.30	2.29	0.39
PEM	0.00	0.00	1.54	0.65	6.98	0.13
SXCN	0.17	0.23	1.33	0.75	5.83	0.13
PVTD	0.09	0.30	3.30	0.30	3.40	0.27
PECH	0.49	0.44	0.89	1.12	3.79	0.22
PVPR	0.46	1.24	2.71	0.37	4.11	0.18
OV202	1.61	0.55	0.34	2.96	2.45	0.33
P4V	3.89	2.36	0.61	1.65	9.88	0.09
SXFA	6.07	7.08	1.17	0.86	5.55	0.13
FPOL	2.75	2.82	1.03	0.97	7.03	0.12
ZDOL	2.55	6.02	2.36	0.42	5.72	0.12
PEI	0.00	0.00	4.62	0.22	8.54	0.09
SPYR	0.00	0.00	2.79	0.36	9.21	0.11

a: Linear solvation energy relationship

h-b: hydrogen-bond

Max h-b acidity (b) with min h-b basicity (a) and min dipolarity (s)
(modelled by b/a and b/s respectively)

There are two strong candidates with large b/a values, SXFA and P4V, but when b/s is considered SXFA stands out as the polymer with maximum h-b acidity properties with minimum h-b basicity and minimum dipolarity. In addition there is only a small contribution from polarizability and the constant has the smallest negative value of the 14 polymers considered (Table 4), this favors higher vapor sorption and larger SAW device signals for all vapors.

Max h-b basicity (a) with min dipolarity (s)
(modelled by a/s)

There are several strong candidates as possible coatings in this category including PEI, PVTD, SPYR and PVPR. All these coatings respond significantly to solute vapors which exhibit h-b acidity such as water and alcohols. PEI provides the largest responses to water but absorbs so much water at high levels of humidity that the SAW device can fail to oscillate. SPYR does not absorb water vapor quite as strongly and operates throughout the full range humidity range. PVPR and PVTD were not considered because of their glassy properties which slow down sorption rates. After some initial experiments we decided against incorporating this type of coating in a 4 SAW array, because of its high sensitivity to changes in water vapor and the inherent difficulties of detecting water released from fires and interpreting these signals with normal ambient changes in humidity, which can be dramatic if the weather changes or if the room is air conditioned.

Max dipolarity (s) with minimum h-b basicity (a)
(modelled by s/a)

The only strong candidate coating in this category is OV202, which showed promise in initial vapor and fire tests, but unfortunately the coating was somewhat volatile and thus could not be included in the final set. OV202 is commercially available from several sources and it may be possible to locate a higher molecular weight sample which would eliminate the volatility problem.

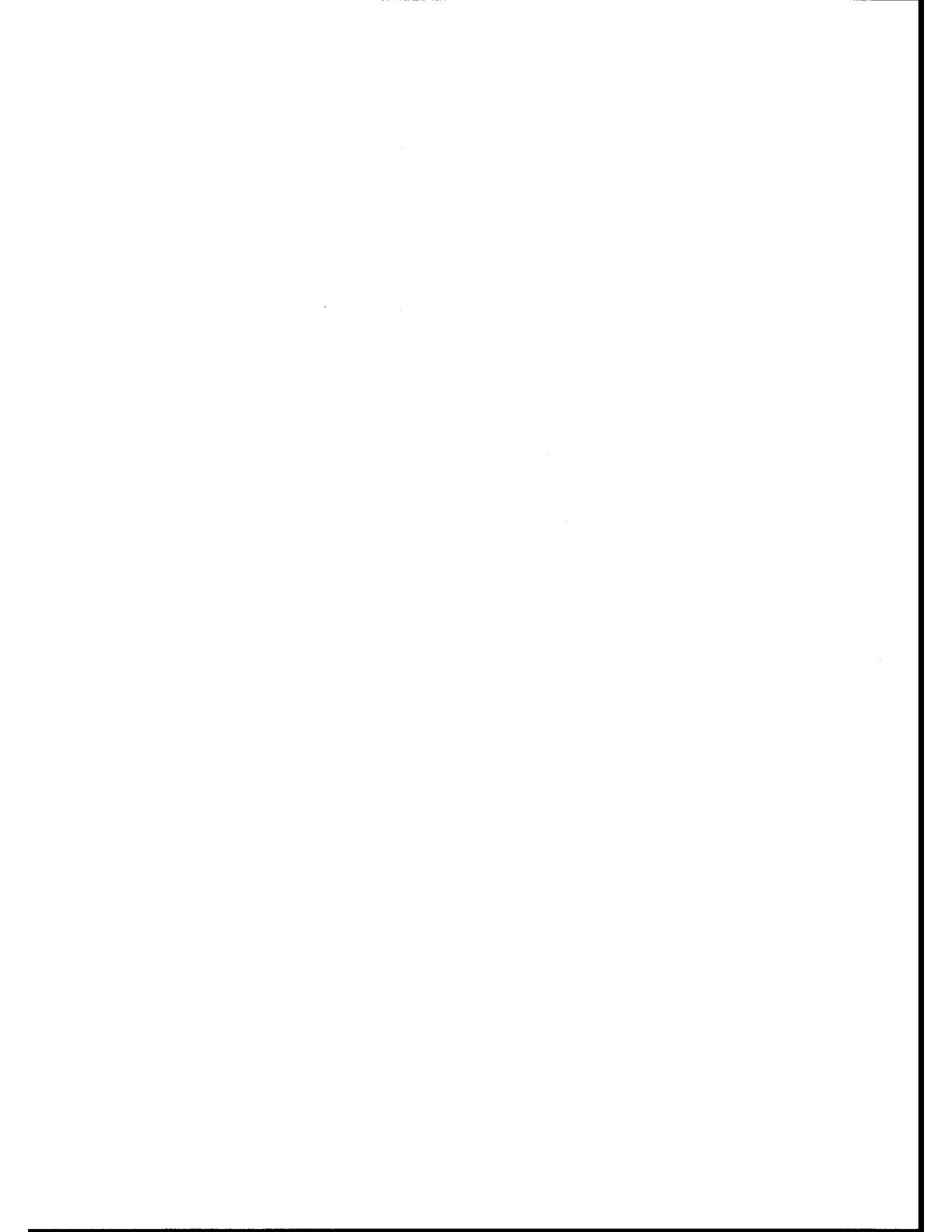
Max h-b acidity (b) with max h-b basicity (a) and max dipolarity (s)
(modelled by b+a+s)

In this category the polymer with the strongest Σ solubility properties is identified. There are several possibilities including P4V, SPYR, PEI, FPOL. However all of these polymers exhibit some dominant solubility property such as h-b acidity or basicity. Ideally a coating with an equal contribution from all the different solubility properties is sought. The polymer which closely fit this description was PECH, and although the size of the numbers are not as large as others it does contain a significant contribution from all areas of solubility properties. It is actually rather a difficult problem to synthesize a polymer repeat unit that behaves both as a strong h-b base and h-b acid. It is not difficult to factor into the polymer repeat unit both strong h-b basic and acidic groups, but normally this does not produce a useful coating because the h-b basic and acidic groups compete for each other as well as for solute vapor. The result being that the strong acidity and basicity properties are lost due to inter and intra molecular interactions between polymer chains. This would also be the case for mixed polymer coatings with h-b acidic and h-b basic solubility properties. One possible solution to this situation would be to coat one end of the SAW oscillator with the h-b polymer coating and the other end with the h-b basic polymer, alternatively the polymers could

be coated on top of one another with some sort of permeable membrane separating them. Another possibility in an array is to combine the signals from a h-b acidic coating and a h-b basic coating with the result that more pattern information might be extracted than just monitoring the signals separately.

Max dispersion(l) with min dipolarity, h-b acidity and basicity
(modelled by $l/(s+b+a)$)

The only strong candidate coating in this category is PIB, with SXPH a distant second choice. Clearly the solubility properties that control the solution of vapor in this coating are primarily van der Waals forces or London dispersion interactions.



APPENDIX B

DATA ACQUISITION AND PATTERN RECOGNITION

Mentor 2.0 is a Windows-based application created using the Visual Basic 2.0 programming environment . Mentor was developed in house at NRL as a control and acquisition interface for the 4-SAW sensor system, to facilitate data logging to IBM compatible computers, plot SAW frequency data for 4 channels in real time, and carry out pattern recognition when vapors are detected. Mentor consists primarily of a main window which displays the numerical values for the frequencies of the 4 SAW sensor array as well as a graphical picture of the relative responses displayed as dots (Fig 7). In another area of the main window, the results of the last successful peak detection are displayed, listing the sensors that peaks were detected on, the height of the peaks above the baseline, and the point number where the peak was detected. Other features include a file management window, a scalable plotting window, and options for interfacing to a variety of field testing units. The overall design and basic features of Mentor were derived from an earlier program, Sawtest, written by Dr D. Dillela in Code 6177 of the Chemistry Division at NRL, which was developed using the QuickBASIC language.

In order to enhance the selectivity of SAW sensor systems arrays of SAW devices have been used in combination with pattern recognition techniques. Mentor 2.0 utilizes a neural network routine for pattern recognition to classify the vapors detected. The neural network toolkit is a collection of routines purchased separately from Ward Systems Inc., and is designed to be accessible from within Visual Basic. The Mentor algorithm is based on a standard probabilistic neural net consisting of an input layer of four neurons, a hidden layer with a maximum of 500 neurons and an output layer of ten neurons. The probabilistic neural network (PNN) is a very simple net

that trains rapidly with large numbers of patterns due to its lack of a back-propagation step. The training set of data for the fire vapor testing contains over 500 patterns (taken from data sets that were corrected for baseline drift), yet the PNN network takes less than a minute to train. Additional patterns can easily be added to the training set from newly acquired field data or by entering pattern values directly. Once trained, the Mentor network classifies the sensor responses automatically while in the Monitor window. The classification can be adjusted using two parameters, the threshold and smoothing factor. The threshold is the minimum frequency each sensor must be above its baseline to allow classification. This helps to prevent incorrect classifications due to noise and gives the pattern time to stabilize. The smoothing factor affects the "fuzziness" of the network classification. Larger smoothing factors blur the distinction between the categories established during training and smaller factors force the net to classify more strictly to the clustering manifested by the training data. A popup window alerts the operator that vapor(s) has been detected and the result of the classification is printed in the window.

The success of the Mentor algorithm is largely dependent upon the quality and quantity of data that was used as the training set. The ideal training set should contain data that represents the fire under a wide variety of conditions. This should include data collected under different levels of ambient humidity and temperature and from different stages of fire development. The vapors evolved and their relative concentrations may change, which in turn could affect the sensor array pattern. Some limited experiments comparing patterns produced in the early stages of smoldering and in medium smoke conditions indicate that the patterns produced are quite similar. However under flaming conditions there might be more significant changes, and if this were the case the SAW sensor system might be able to distinguish between a smoldering and flaming fire. If the variations in patterns produced under different

conditions is small then the system can be trained to search for a more precise pattern which reduces the possibility of a false alarm. However if the pattern variation is significant, but not large enough for a separate classification then the system would have to be trained to identify a pattern that allows for more flexibility in its identification.

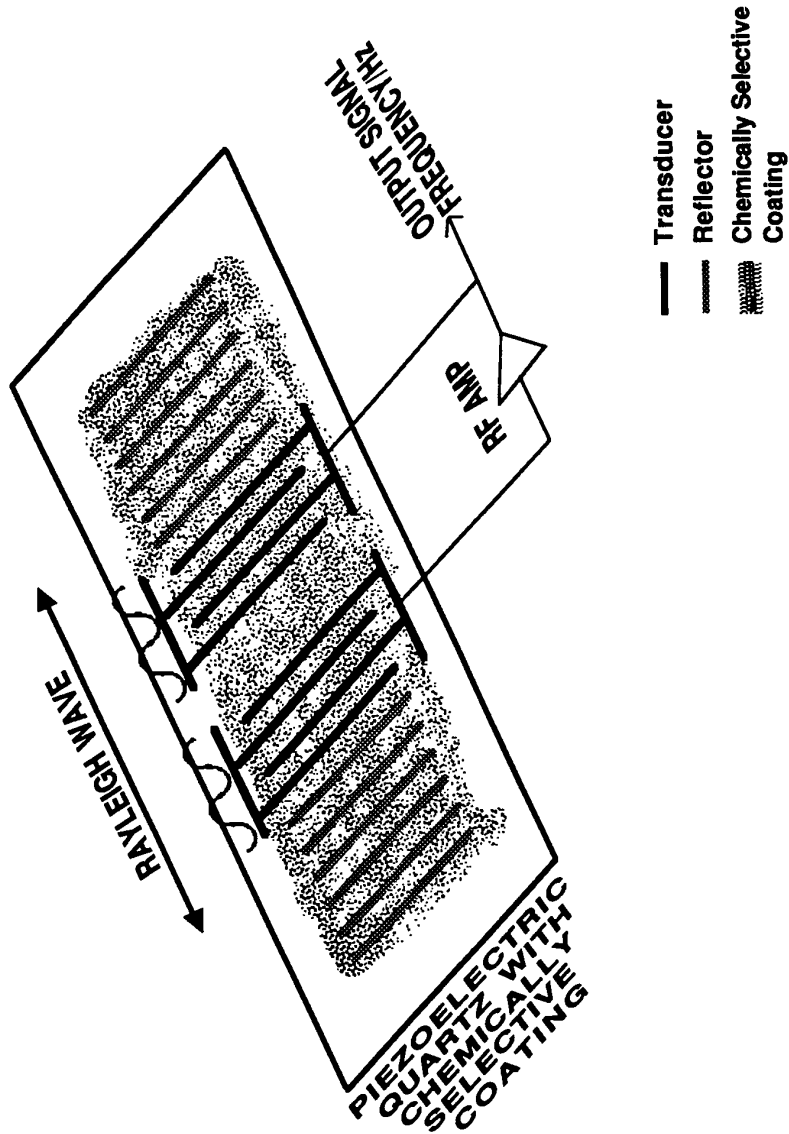
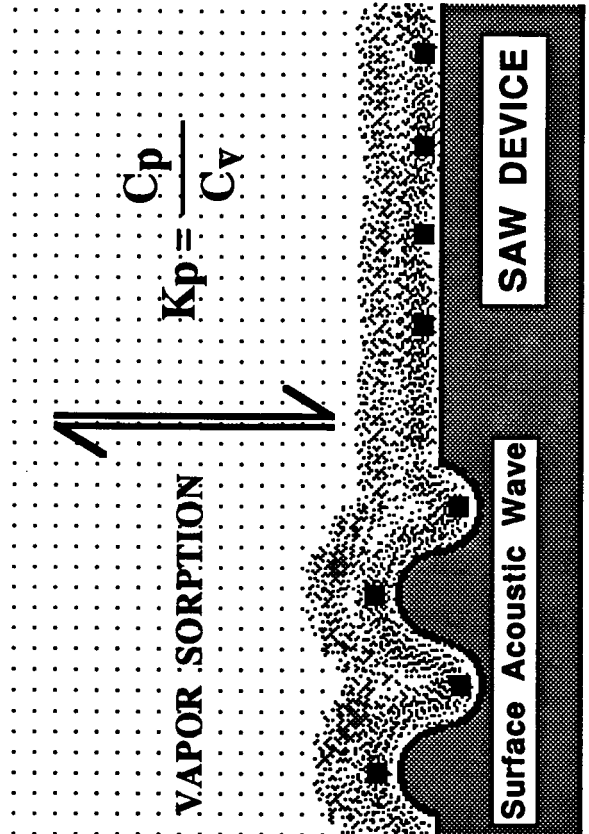


Fig. 1
SURFACE ACOUSTIC WAVE RESONATOR
WITH CHEMICALLY SELECTIVE COATING
(SAW RESONATOR)

**CHEMICALLY
SELECTIVE COATING**

**PIEZOELECTRIC
QUARTZ CRYSTAL**



**Fig. 2 REVERSIBLE VAPOR SORPTION PROCESSES IN A
POLYMER COATED SAW DEVICE**

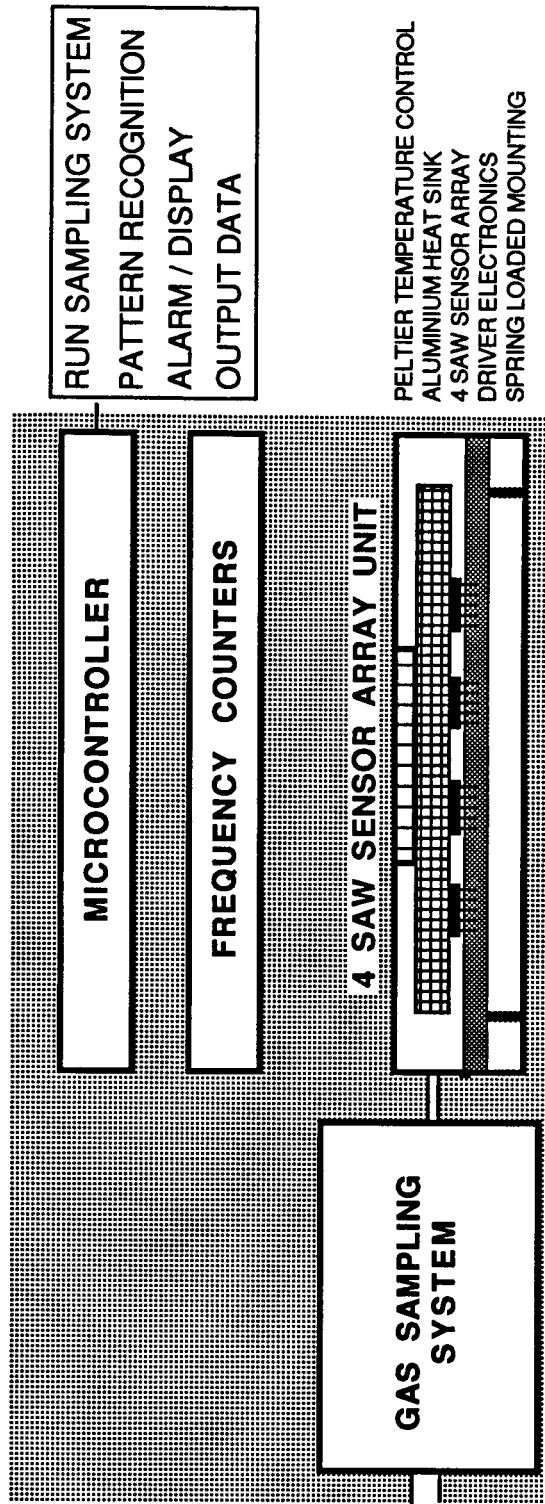


Fig 3 SAW "FIRE THREAT" SENSOR SYSTEM

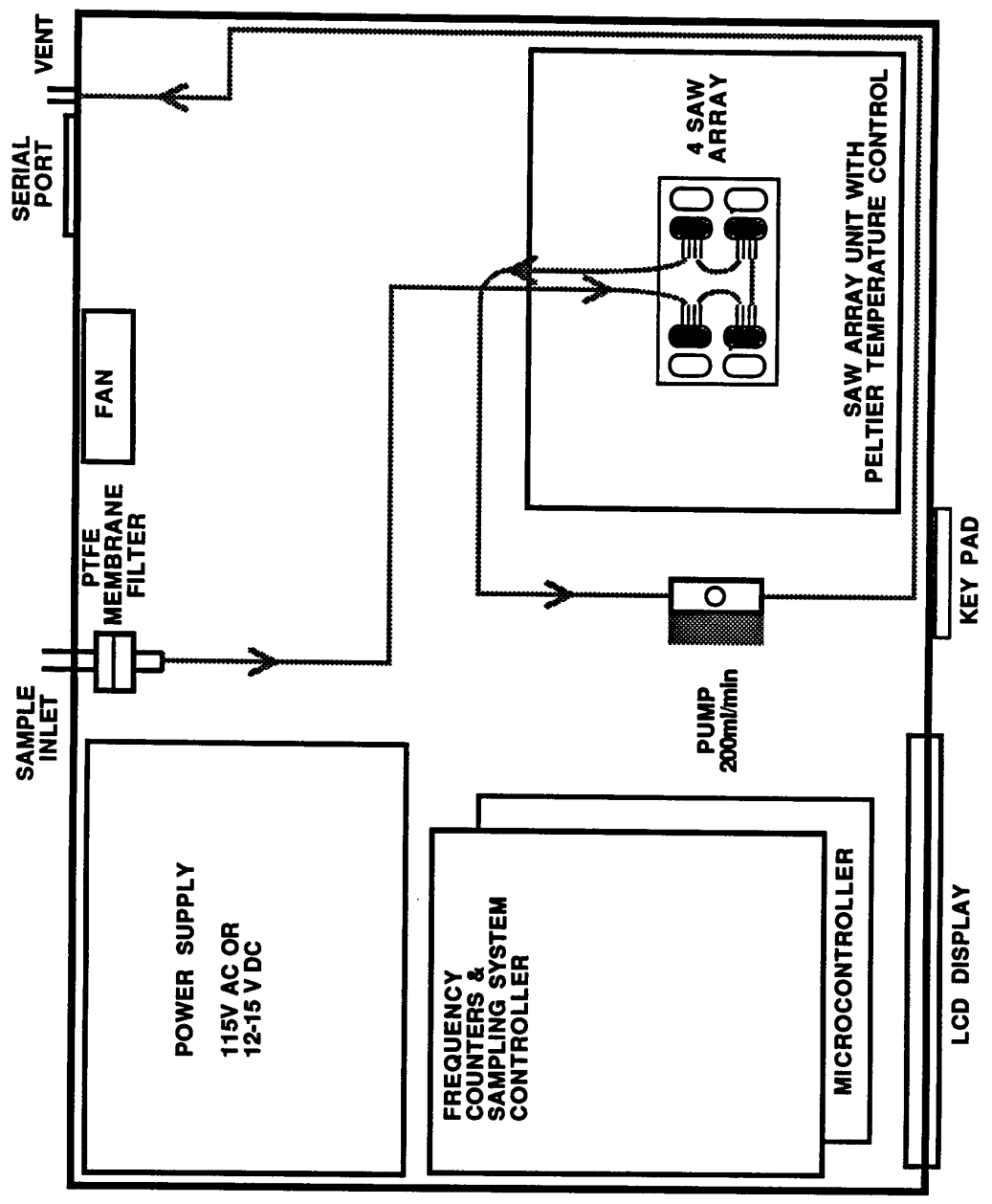


Fig 4 SAW "FIRE THREAT" SENSOR SYSTEM

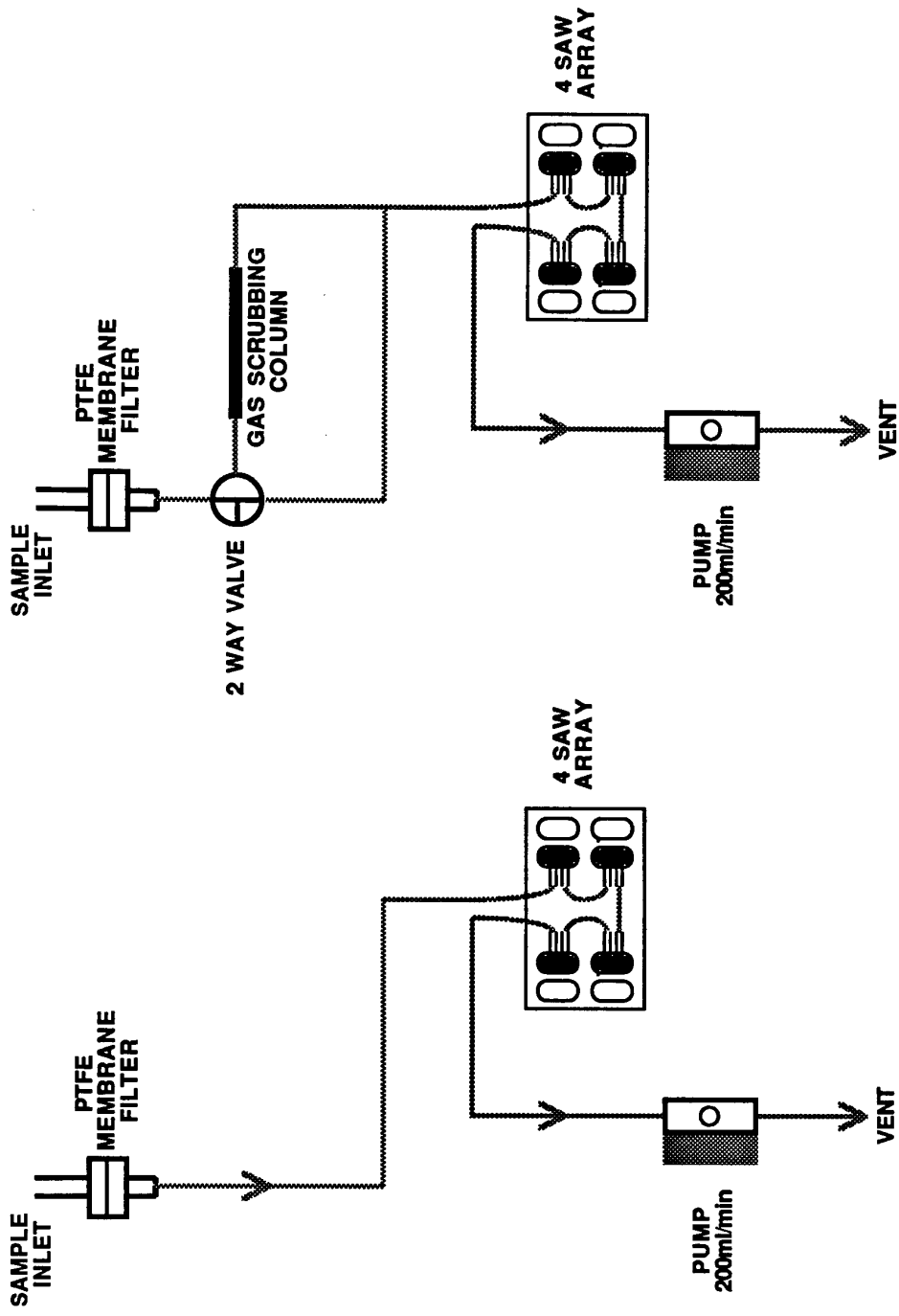


Fig 5b

Fig 5a

AMBIENT GAS SAMPLING SYSTEMS

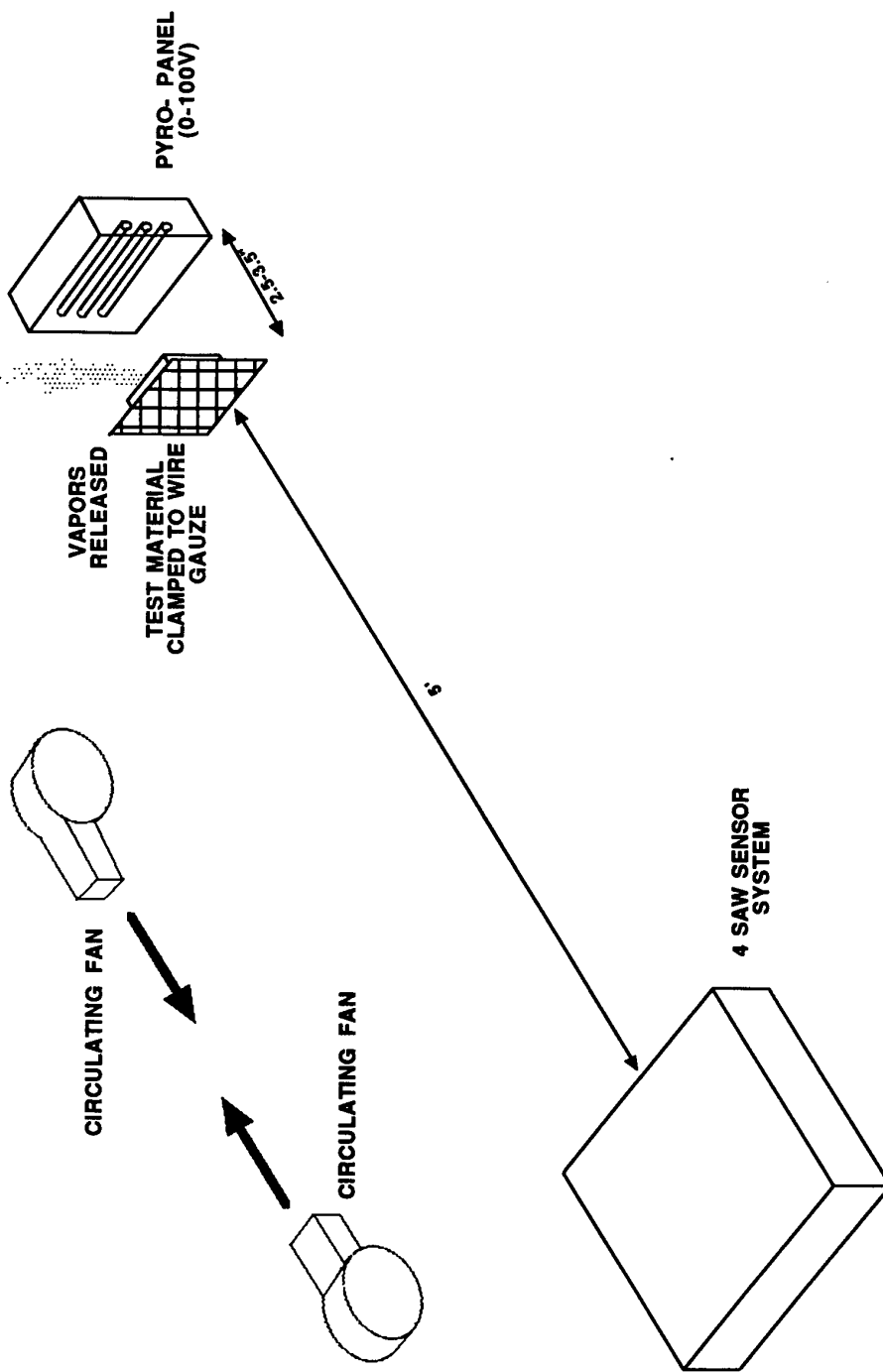


Fig 6 SCHEMATIC DIAGRAM OF EQUIPMENT USED IN 177ft³ FIRE CHAMBER AT CBD-NRL FOR FIRE THREAT TESTING AND 4 SAW SENSOR SYSTEM EVALUATION

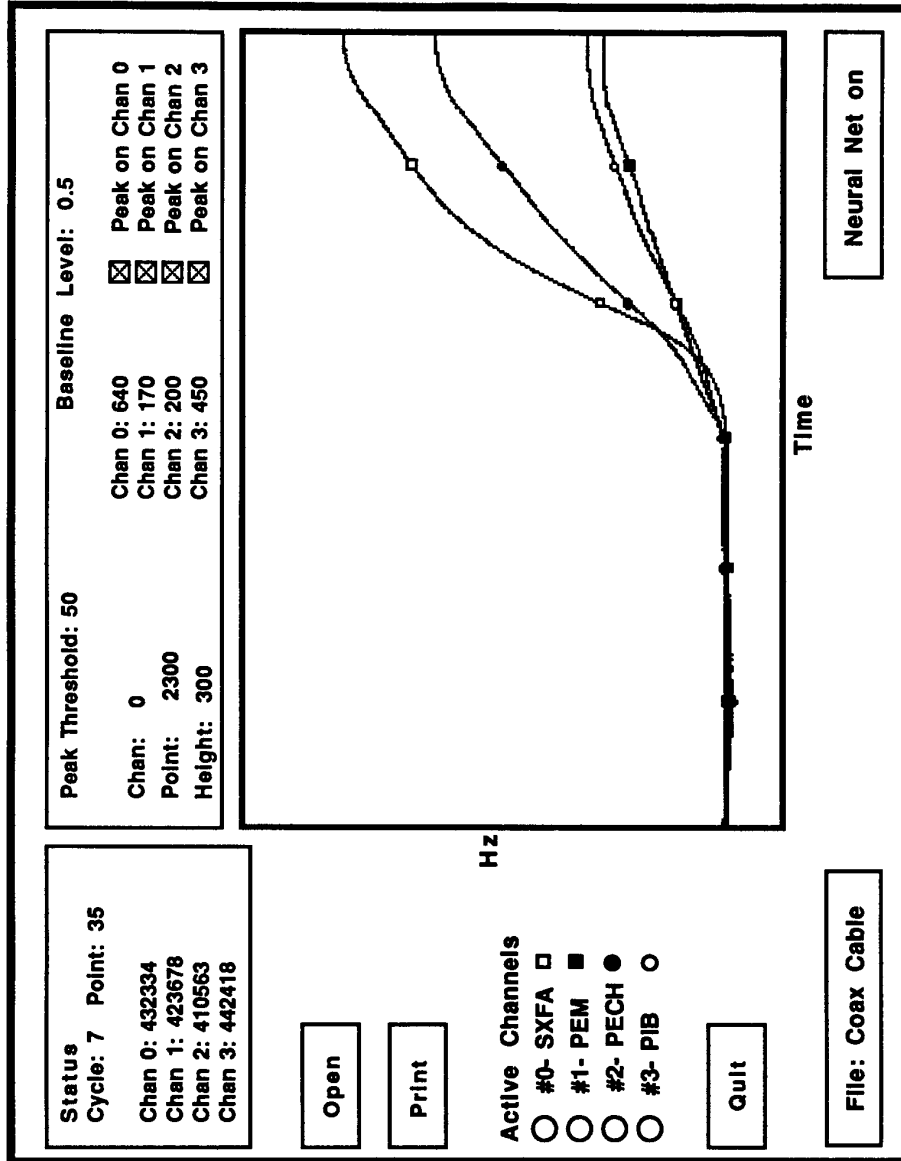


Fig 7 Mentor 2.0 Screen Display

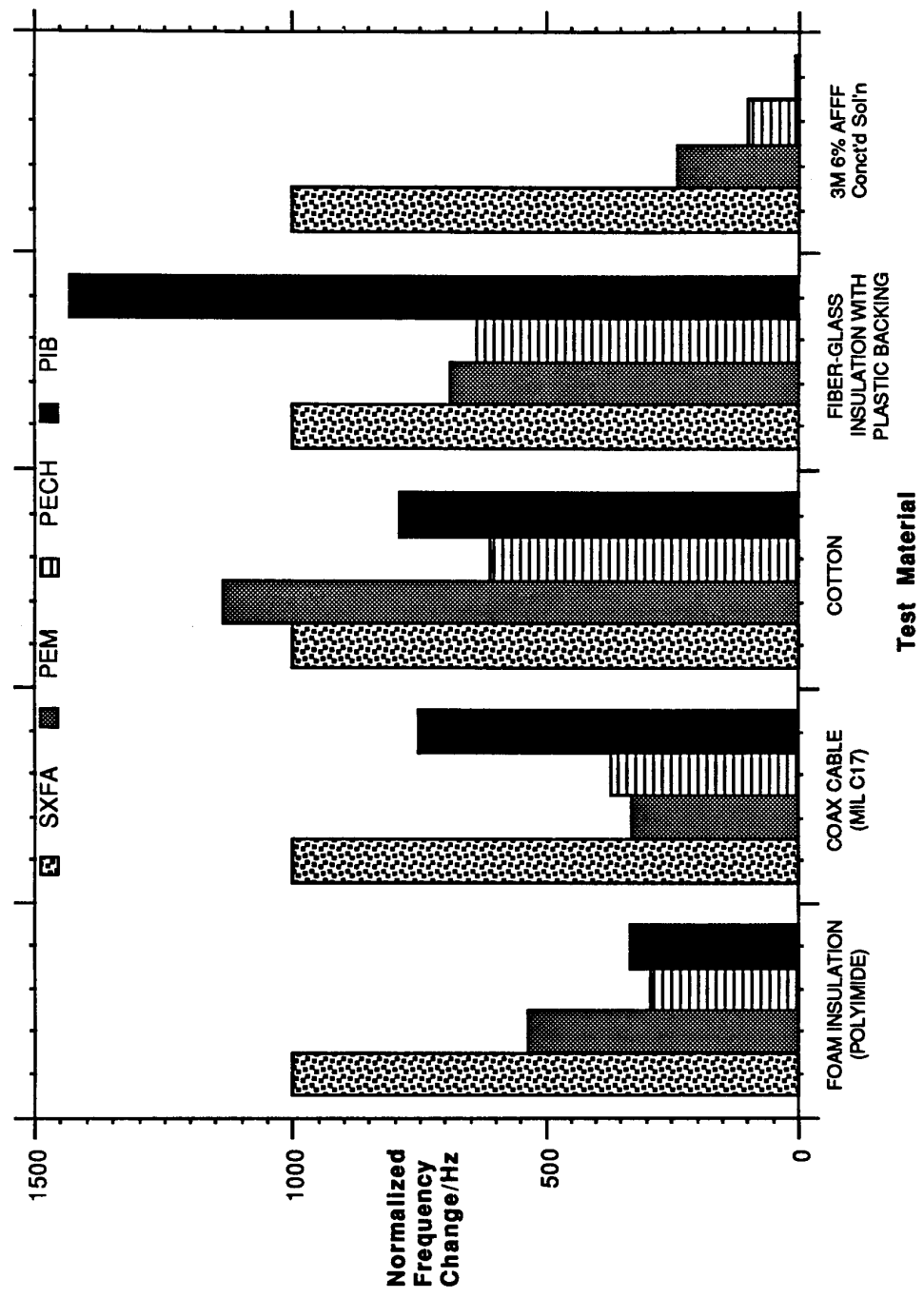


Fig 8 4 SAW Array Pattern Responses Compared For 4 Heated Materials and AFFF a Possible Interferent

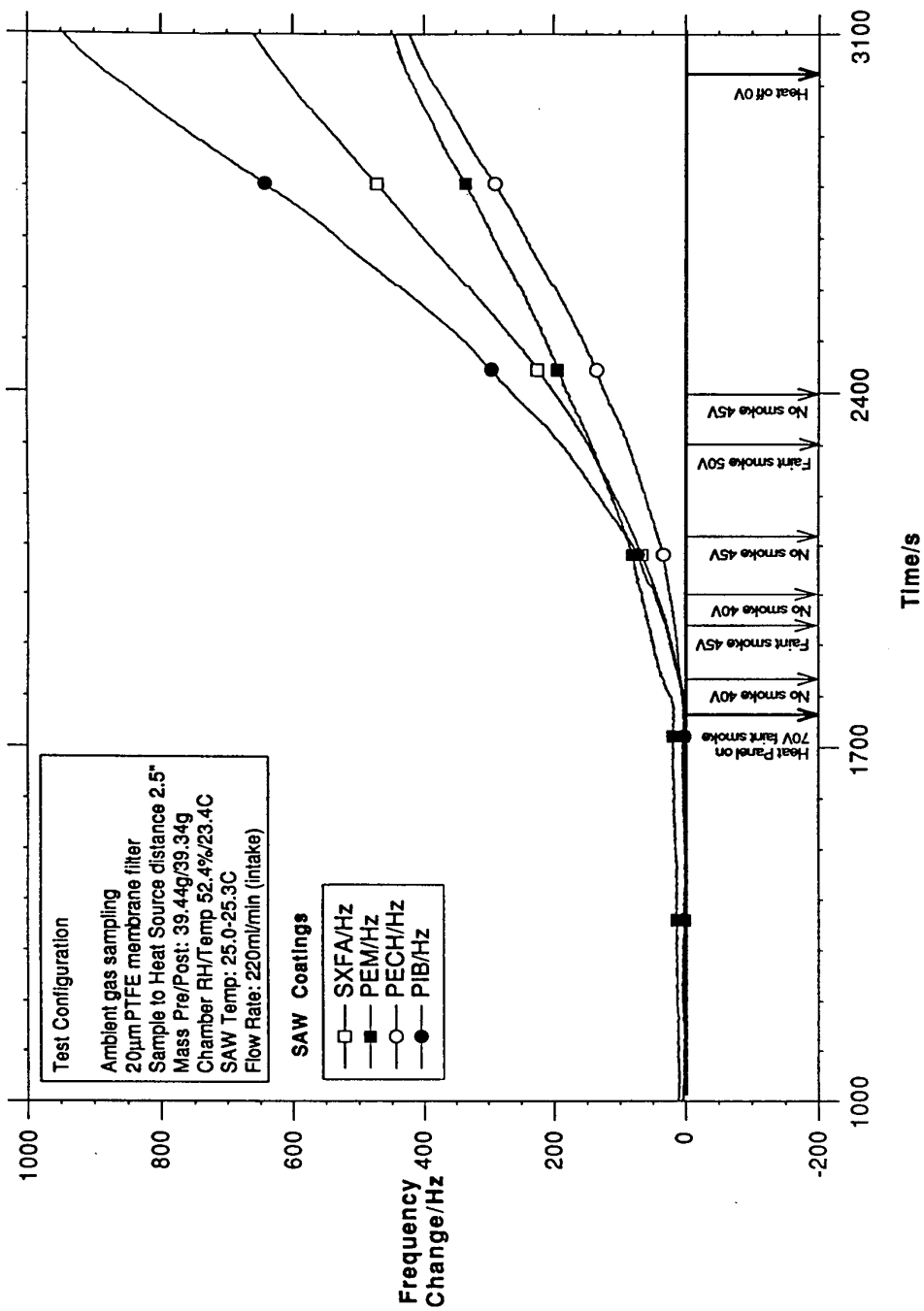


Fig 9a Smart 4 Sensor Array Response to Heated Fiber Glass

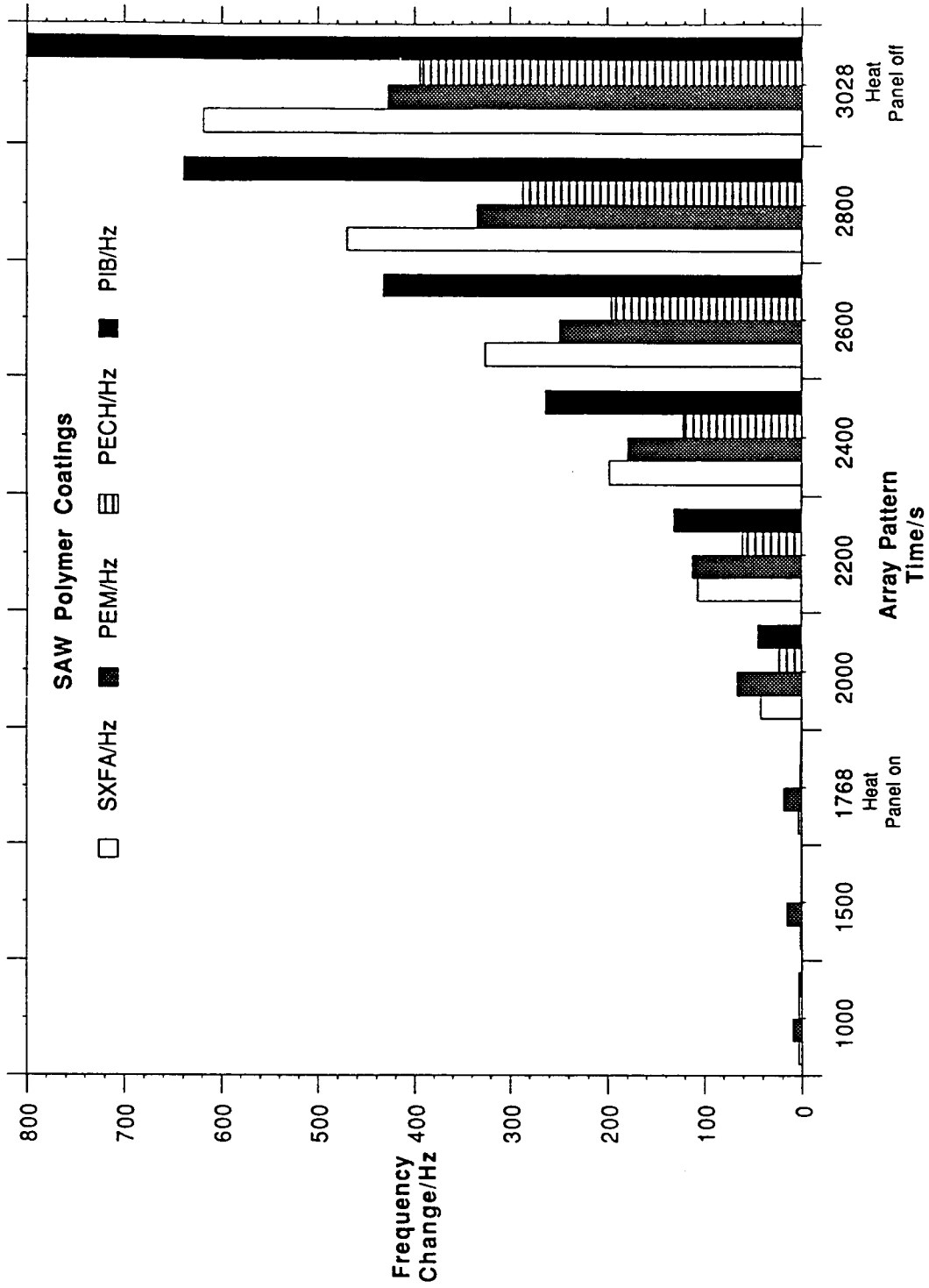
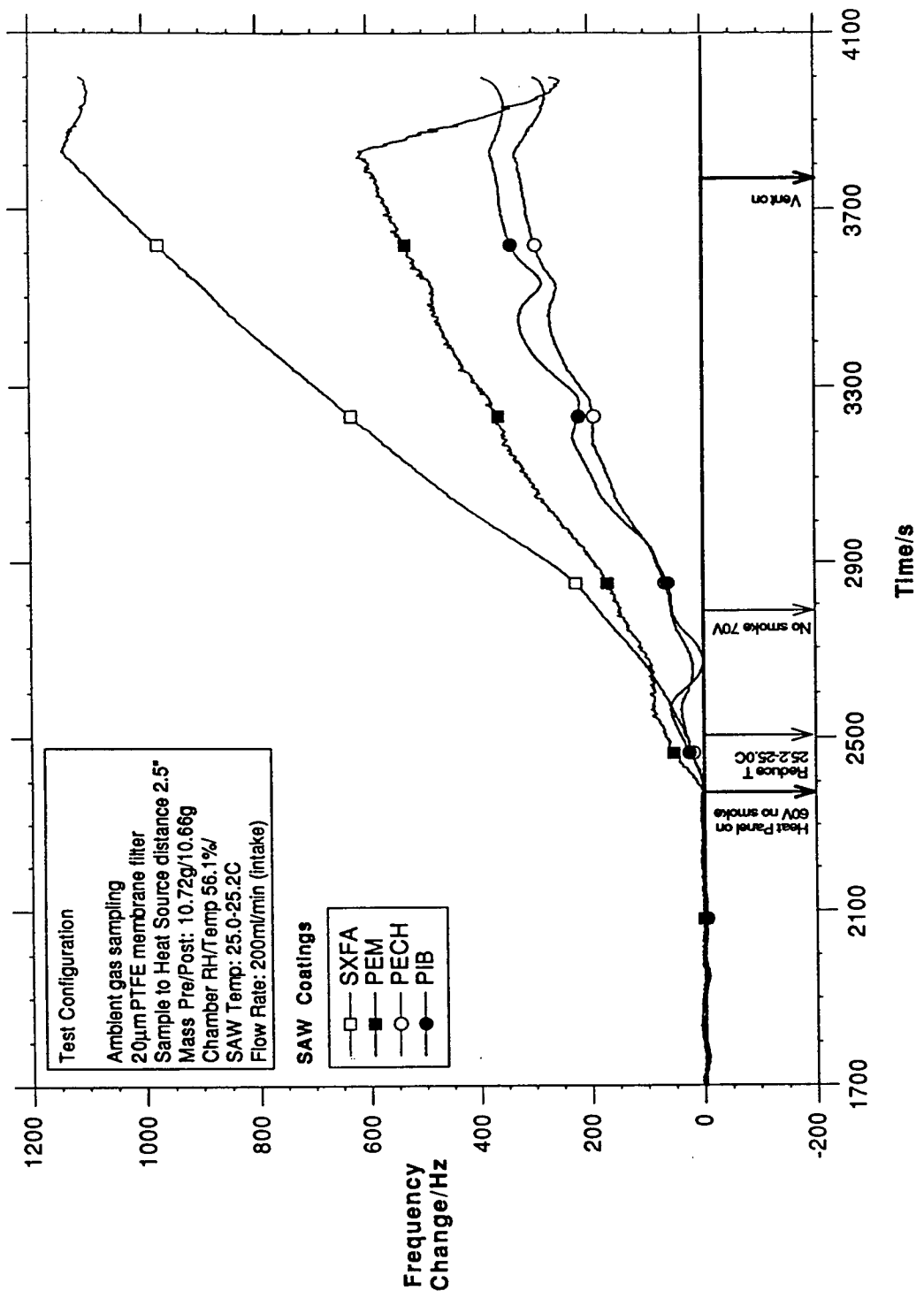


Fig 9b 4 SAW Array Pattern Response to Heated Fiber Glass



SMART 4 Sensor Array Response to Heated Insulation Foam

Fig 10a

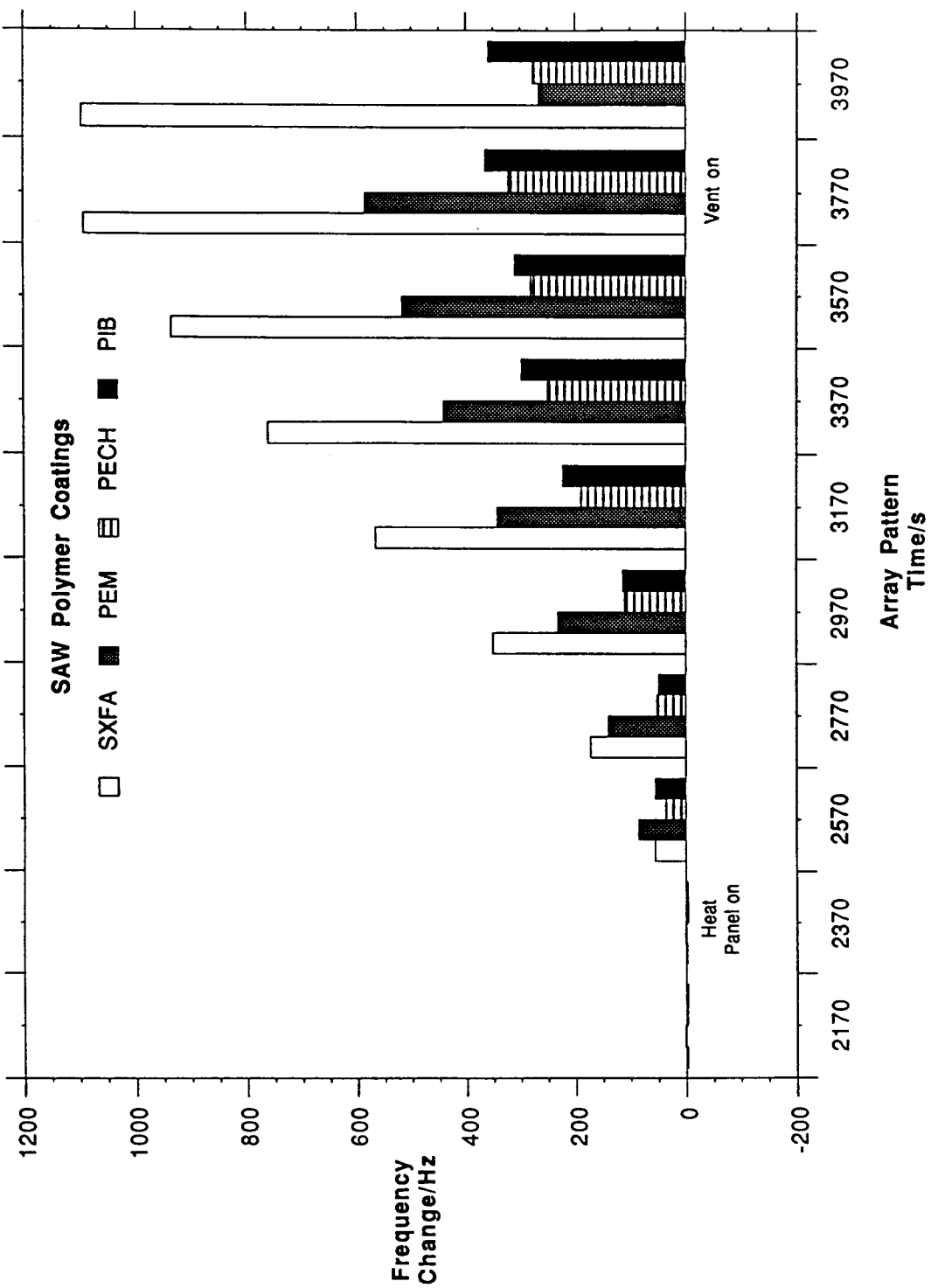


Fig 10b 4 SAW Array Pattern Response to Heated Insulation Foam

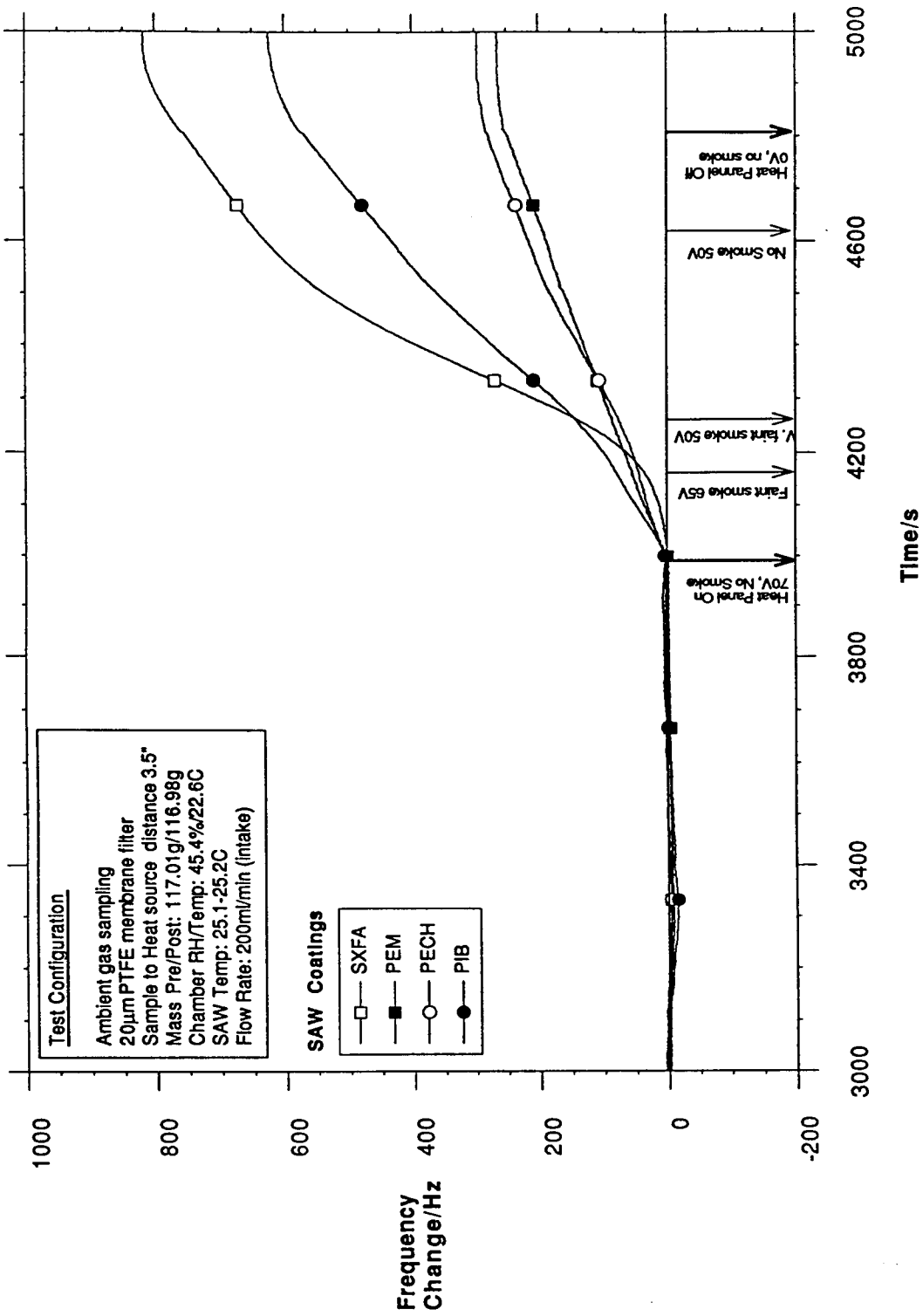


Fig 11a Smart 4 Sensor Array Response to Heated Coax Cable Mil C17/29-RG59

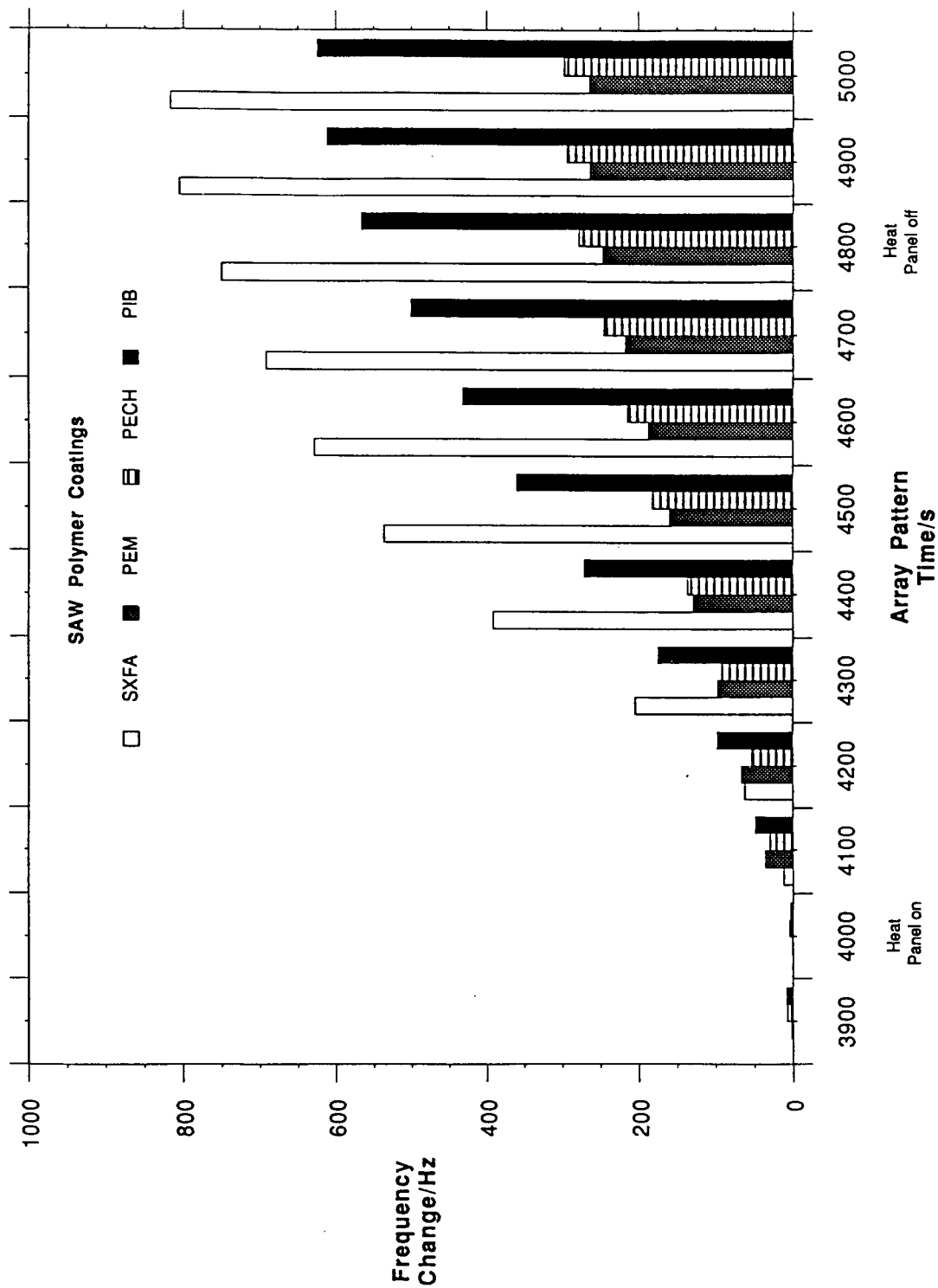
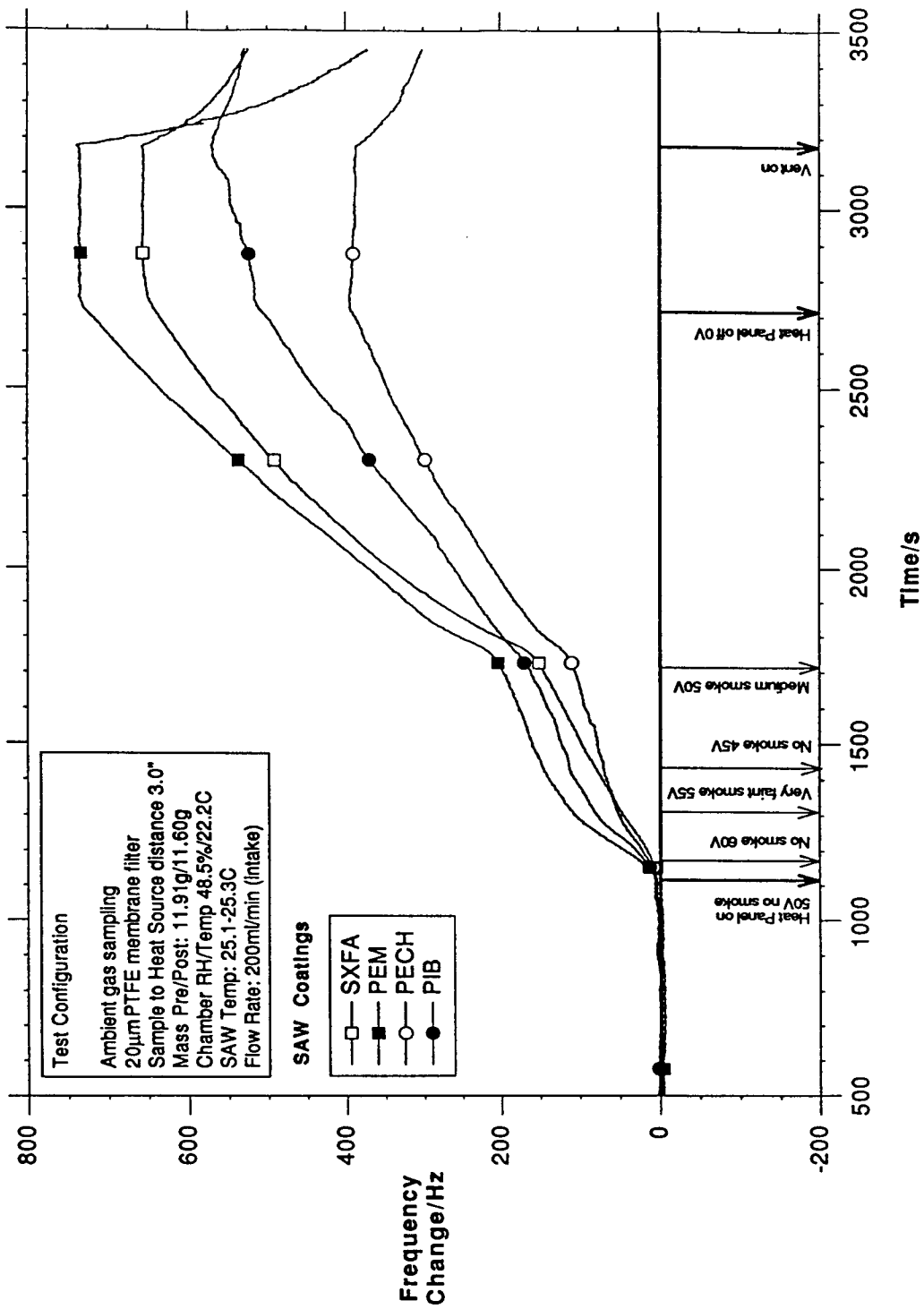


Fig 11b 4 SAW ARRAY Pattern Response to Heated Coax Cable Mil C17/29-RG59.



Smart 4 Sensor Array Response to Heated Cotton

Fig 12a

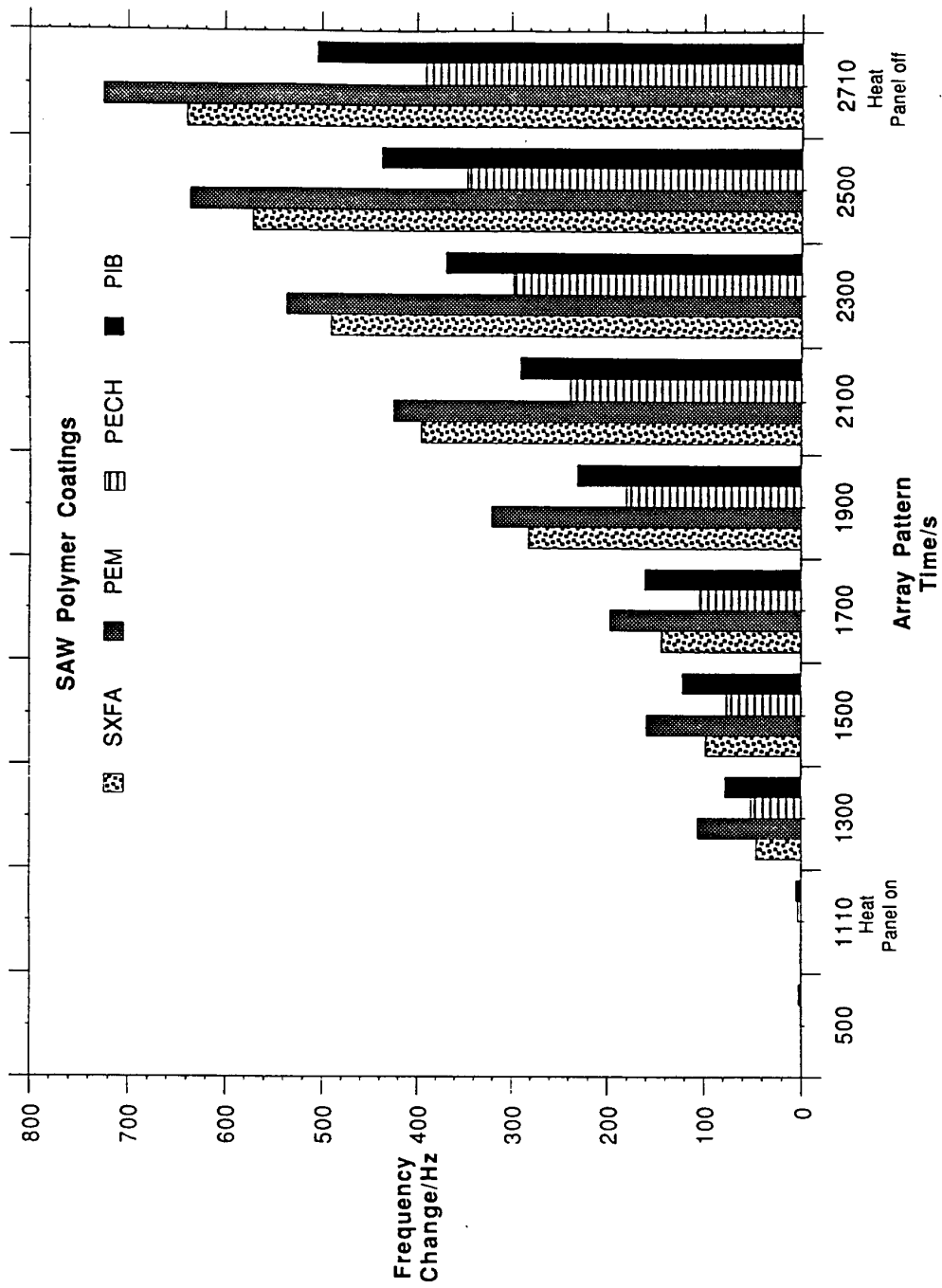


Fig 12b 4 SAW Array Pattern Response to Heated Cotton

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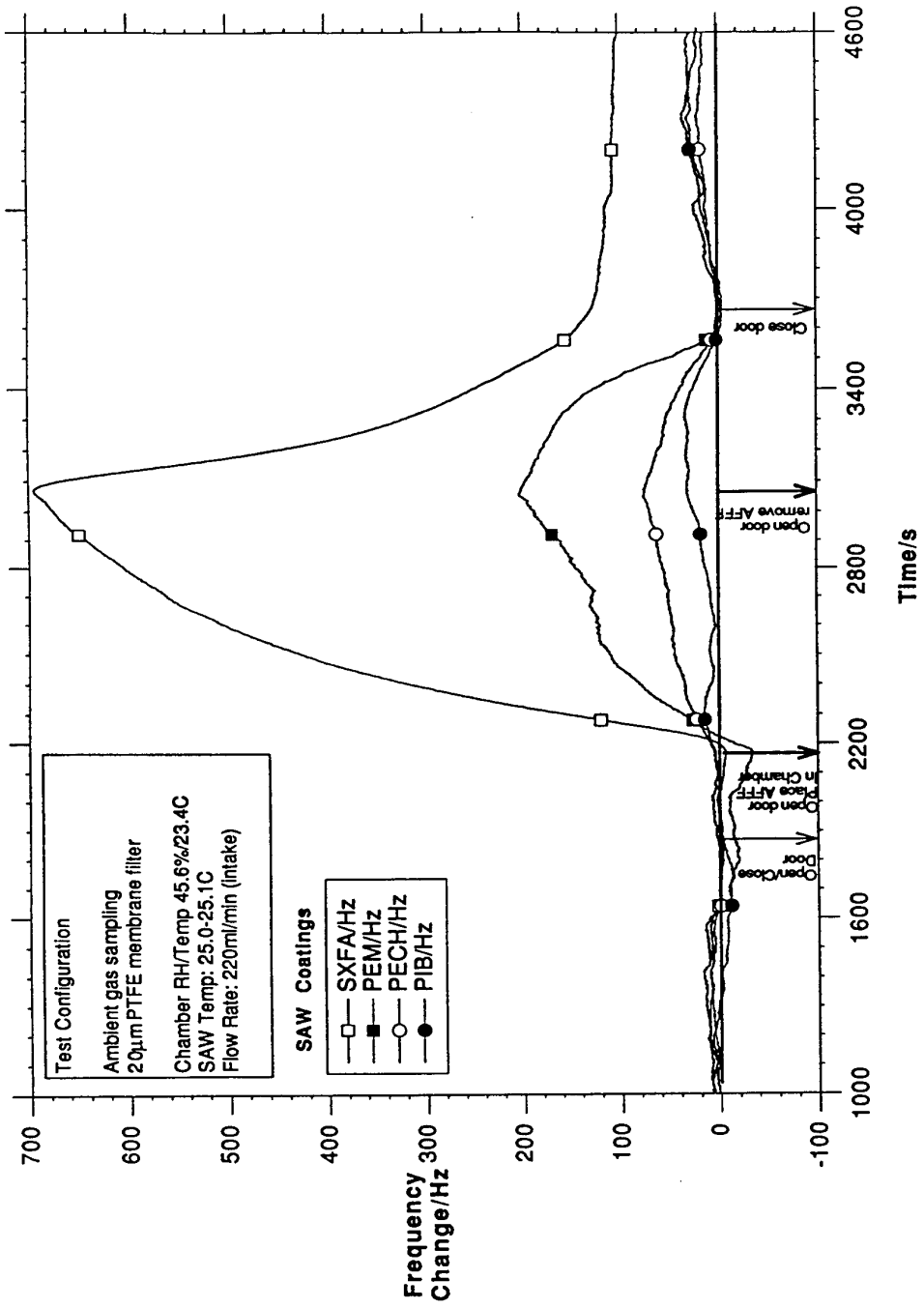


Fig 13a Smart 4 Sensor Array Response to 3M 6%AFFF Fire Fighting Solution

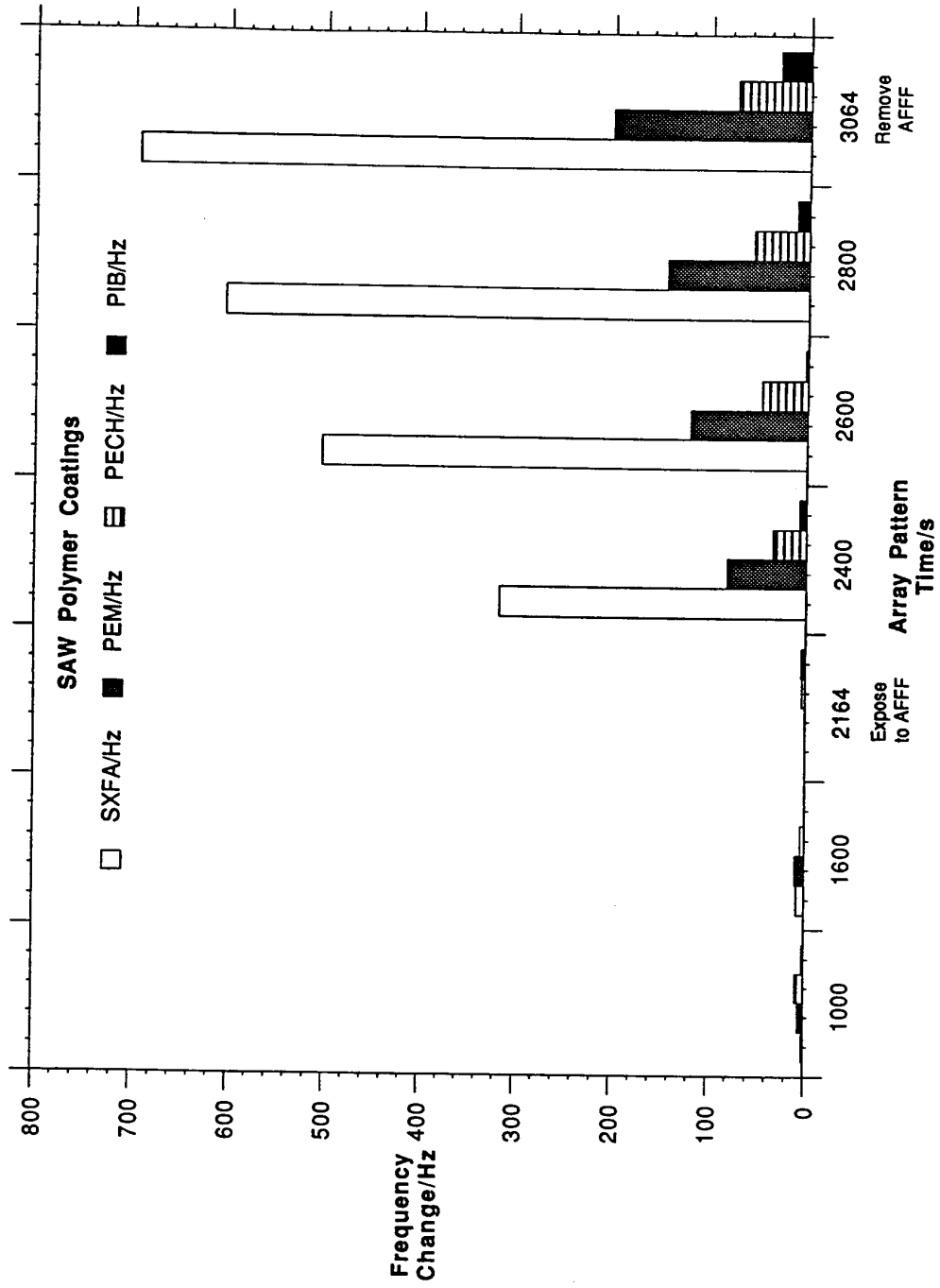
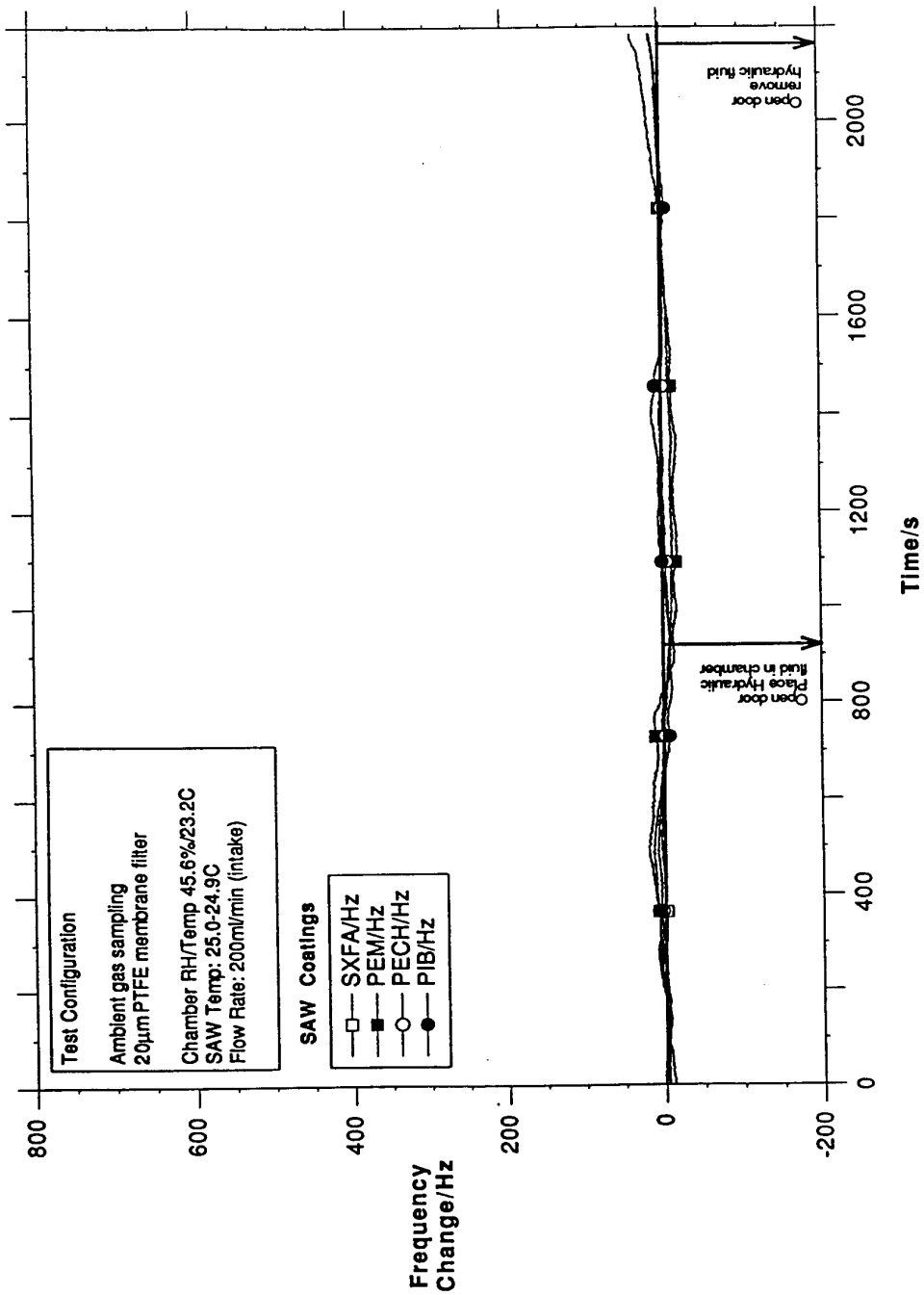


Fig 13b
4 SAW Array Pattern Response
to 6% AFFF Fire Fighting Solution



Smart 4 Sensor Array Response to Fyrquel Hydraulic Fluid

Fig 14a

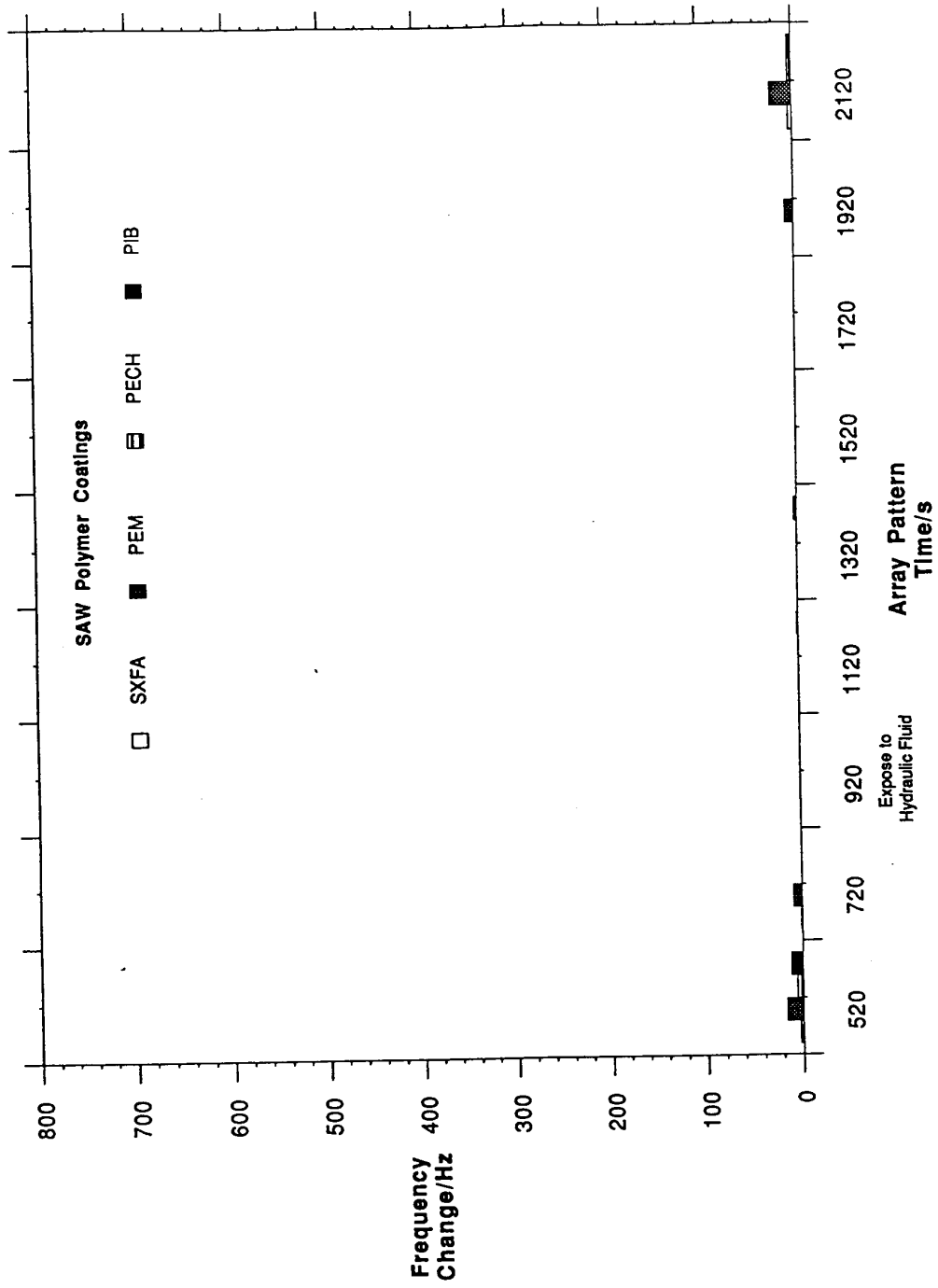


Fig 14b **4 SAW Array Pattern Response to Hydraulic Fluid**

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